PB-230 518

# MASS TRANSFER IN DROPS UNDER CONDITIONS THAT PROMOTE OSCILLATION AND INTERNAL CIRCULATION

Gus L. Constan

Case Institute of Technology

Prepared for:

Public Health Service

1961

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# MASS TRANSFER IN DROPS UNDER CONDITIONS THAT PROMOTE OSCILLATION AND INTERNAL CIRCULATION

## BY GUS L. CONSTAN

REPRODUCED AS APPENDIX A

for

"BASIC STUDY OF AIR POLLUTION
CONTROL WET SCRUBBERS"

Seymour Calvert
January 13, 1961

Chemical Engineering Division

CASE INSTITUTE OF TECHNOLOGY
CLEVELAND, OHIO

U. S. Public Health Service Research Grant S-84

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# MASS TRANSFER IN DROPS UNDER CONDITIONS THAT PROMOTE OSCILLATION AND INTERNAL CIRCULATION

A Thesis Submitted to
Case Institute of Technology
in Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by

Gus L. Constan

1961

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## ABSTRACT

Single drops supported on hypodermic tubing have been studied in a wind tunnel to determine the effect of drop oscillation on mass transfer. The systems studied for the case where internal resistance controls consisted of absorption of $SO_2$ gas by drops of glycerine, propylene glycol, and ethylene glycol. The results can be expressed in terms of effective diffusivity.

No significant effect was noted in glycerine, whereas the glycols gave effective diffusivity values of 2-8.

Frequencies, amplitudes, and internal circulation velocities in the drops were studied by cinematography, and are compared with predicted magnitudes.

The effect of oscillation on external mass transfer coefficients was studied by sublimation of naphthalene spheres. In the cases where the vibrational velocity was less than the stream velocity, no effect was noted; this is in agreement with heat transfer studies.

A technique has been developed for studying the effect of internal circulation on effective diffusivity, using forced circulation through a drop suspended on hypodermic tubing. A "pseudo-film thickness" is determined as a function of circulation velocity, and presents a means of predicting effective diffusivity. This technique

has been demonstrated for the system $SO_2$-$H_2O$, giving results in fair agreement with the correlation of Garner and Lane[17]. (M)

# ACKNOWLEDGMENTS

The author wishes to express his gratitude for his wife's understanding and encouragement throughout this entire study. The guidance and the numerous helpful suggestions of Professor Seymour Calvert have proven invaluable to this work. The generous aid of Dow Corning Corporation and the U. S. Department of Health, Education, and Welfare in making this work possible is hereby acknowledged.

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# INTRODUCTION

The transport phenomenon of mass transfer between drops and their surrounding medium has been the subject of many studies. Most of this work has been carried out on freely falling drops through a gas or another liquid phase.

Falling drops generally undergo distortion from the spherical shape and at times exhibit internal circulation. This behaviour is more prominent in the case of a drop falling through a gas, where the fall velocity is great. One would expect that transport rates would be enhanced if a greater contacting area and/or bulk transport within the drop occurred. Various observers have confirmed this result in cases where deformation of the drop occurred or where internal circulation existed.

Internal circulation takes on greatest significance when liquid phase resistance is controlling. In previous studies of falling drops this phenomenon was most pronounced at the time of drop formation and disengagement, followed by rapid damping during the drop fall. The short duration of high circulation rates in these cases makes their measurement impractical.

In the case of supported drops, the drop distortion and circulation is caused by the action of the gas stream and would persist as long as the gas stream was sustained. Thus, an extended duration is provided for studying the behaviour of the drop.

This study is based on single drops supported on tubular elements and exposed to a stream of gas so as to create drop oscillation and internal circulation. An auxilliary technique of forced circulation through a drop suspended on tubing has been employed to predict the effect of internal circulation.

# THEORETICAL AND EXPERIMENTAL BACKGROUND

## A. INTERNAL CIRCULATION IN DROPS

Internal circulation is the result of drag exerted on a moving drop but may also be caused by oscillatory distortion. The effect of internal circulation would be expected to increase mass transfer rates over those of pure diffusion, and such appears to be the case.

The formation of vortices in fluid spheres in motion was postulated by Hadamard[21] before this phenomenon had been observed. However, his case was for "creeping" motion and spheres of zero surface tension. Kronig and Brink[27] calculated the effect of this circulation under the influence of gravity on mass transfer for the case of negligible surface tension, Reynolds Number less than one, and no continuous phase resistance, and predicted a maximum increase in rate of 2.5 over that of pure diffusion. Bond and Newton[3] presented a correlation to take into account surface tension, and thus provided a means of calculating the critical diameter at which circulation first begins. Elzinga and Banchero[12] applied the Kronig and Brink relationship to also include continuous phase resistance to heat transfer in a liquid-liquid system. Handlos and Baron[22] presented a theoretical treatment of an irreversible thermodynamic process at high Reynolds Numbers, and arrived at a correlation involving the Peclet Number. However, this correlation is limited to liquid-liquid systems where viscosities of the phases are of the same order of magnitude, and fails for cases of gas absorption. Calderbank and Korchinski[4] modified the Kronig and Brink equation by including a correlation factor R as a multiplier of molecular diffusivity. This factor R takes on a value of one for stagnant drops, 2.7 for circulating drops at Reynolds Numbers below one, and is a function of the Peclet Number at turbulent circulation.

Hughes and Gilliland[23] in a very extensive study of drop mechanics presented a treatment of internal circulation caused by the drag exerted when gas flows by a drop and extended the treatment to include internal circulation caused by oscillating distortion for streamline flow.

Actual experimental observation of the effects of internal circulation was first reported in a liquid-liquid system by Sherwood[35] who noted increasing mass transfer coefficients with increasing drop size, attributing the increase to greater circulation in the larger drops. Several observers[4, 24, 31] in studies with falling drops have obtained results in agreement with values predicted by Kronig and Brink. Garner[15] observed circulation by means of high speed photography of absorption of a material producing a color pattern in the drop; he also determined the point of incipient circulation for various kinds of drops as a function of Reynolds Number[18]. El Wakil[11] used powdered aluminum in fuel oil drops suspended on a wire and by means of high speed photography was able to get an approximate measure of the circulation velocity in the drops. Most recently Garner and Lane[17], using a similar velocity technique on liquid drops freely suspended in a gas stream, arrived at a correlation between internal Reynolds Number and "effective diffusivity" as defined by Calderbank and Korchinski[4]. The correlation was based on the maximum circulation velocity that occurred shortly after the drop release. Increases in rates up to 80 times over that of pure stagnant diffusion were noted for carbon dioxide absorption in water at the point of maximum circulation velocity, and lower values for other systems.

Investigation of the effect of liquid "jet" velocity during the period of drop formation and growth period have been made by a number of observers[6, 10, 20].

A Reynolds Number of 40 to 50 for flow inside a drop is proposed as a criterion for the point at which the "jet" or circulation effect becomes important.

A recent study[12] of heat transfer to drops showed that internal circulation can also affect the continuous phase resistance. The motion inside the drop reduces shear at the drop surface and, thus, decreases the hydrodynamic boundary layer across the drop.

## B. DISTORTION AND OSCILLATION OF DROPS

Non-stationary distortion of a drop may increase rates of mass transfer by these mechanisms: (1) by increasing the surface area as compared to a sphere, (2) by promoting internal circulation in the drop, and (3) by reducing the gas film resistance.

Visual observations of distortion have been reported for free-falling drops by various writers. The most complete recent study is by Finlay[13]. Only one such study has been reported on observation of oscillation of suspended drops[9, 23]. The distortions are of two basic types: those of an equilibrium or permanent nature, and those of an oscillatory nature resulting from vibrations about this equilibrium position. Some of the oscillations are started by the elongation which occurs when the drop breaks loose from the forming tip. Others result from the motion of the surrounding fluid, particularly in the wake behind the drop, where intermittent shedding of the vortices occurs. Hughes and Gilliland[25] postulate that the oscillating distortion is caused by the pressure difference across the surface which is supported by the surface forces, while Haydon and Davies[9, 23] attribute the oscillation to variation of surface tension forces about the drop surface caused by localized concentration differences.

The conventional approach to date has been to assume that the distorted shape is a spheroid, with its axis in the direction of motion, oscillating around an oblate or prolate form. Visual and photographic observations verify this assumption in a gross sense (the spheroid is not symmetrical) and indicate that the ratio of axes in all cases reported lies between 1 and 2[13]. It can be shown that the surface area of these spheroids is no more than 10% larger than that of equivalent spheres. For unsupported drops it is evident that the increased area due to oscillation has only a minor effect on mass transfer. A larger effect would be anticipated in supported drops where gross distortion might occur; but, even then an area increase of more than 100% could hardly be expected. This, then, discounts the mechanism of increased surface area as a major means of causing significantly large increases in mass transfer ratio.

The effect of internal circulation on mass transfer to drops when internal resistance is controlling has been discussed in Section A and is known to be significant. The only treatment of internal circulation caused by oscillatory distortion is by Hughes and Gilliland[25] giving an order of magnitude of circulation velocities as a function of distortion amplitude for streamline flow. This is for a free drop and is based on Lamb's treatment[29] of a sphere oscillating between an oblate and prolate spheroid. The mathematical treatment of the dynamics of a randomly oscillating pendant drop is extremely complex, and only Davies and Haydon[9] have attempted this. By deriving equations of motion for oscillation of pendant liquid drops in another liquid, they attempt to predict frequency of oscillation as a function of physical properties. However, they do not relate this to circulation velocity, and the frequencies of oscillation appear to be no more accurate than what would be predicted by the simpler case of Lamb[29].

The third mechanism, which is to decrease the gas phase resistance, would depend upon the oscillations and distortions of the sphere cutting across the laminar sublayer of the gas film. How significant the effect would be on the outside resistance would depend on factors such as amplitude and frequency of oscillation, thickness of laminar sublayer, how rapidly the sublayer deforms and reforms, and physical properties of the systems. Studies on this mechanism have been restricted to heat transfer from wires on cylinders[2, 28, 30, 36] and indicate that the effect is dependent on the relative magnitude of oscillatory velocity to stream velocity.

Generally speaking, in the case of free-falling drops, distortion and oscillation manifest themselves as end effects, quickly damping out. They represent a large fraction of the total absorption process, and various means have been employed to separate their effect from the main contact period. In the case of supported drops, where oscillation can be maintained for extended periods of time, the end effects become of much less relative importance.

Oscillation and deformation of drops can be affected by the presence of surface active agents. Many reports with varying interpretations of the results appear in literature. Considerations of surface active agents is beyond the scope of this study.

## OBJECTIVES AND SCOPE OF WORK

The specific aim of this study was to define the relationship of mass transfer to oscillation and internal circulation for the case of gas absorption by supported liquid drops. To this end, it was necessary to determine how drops oscillate under different conditions, and how internal circulation behaves in oscillating drops.

Literature tells us that oscillation has only small effects on surface area and thus does not contribute significantly to mass transfer by this means. Studies on heat transfer indicate that the effect of oscillation on outside heat transfer coefficients should be small or negligible under the conditions being considered and we might expect this to also apply to mass transfer. Finally, all previous work indicates that internal circulation is the significant mechanism.

From the literature it is possible to make rough estimates of frequency and amplitude oscillations, based on free-falling spheres. This serves as a starting point. The relationship between oscillation and internal circulation is inadequately characterized, but one may calculate an approximate circulation velocity as a function of oscillation as well as an approximate velocity due to skin friction. Finally, relationships exist that may be used to predict in a limited fashion the effect of internal circulation on mass transfer coefficients.

The above summary, then, points out the areas of significant effects and presents means to make preliminary approximations based on severely limiting assumptions. These approximations serve as a guide to the experimental work that is necessary to establish the actual relationship of drop oscillation and internal circulation to mass transfer in drops.

The experimental work to be described in the subsequent sections checks the validity of applying the heat transfer conclusions on effect of drop oscillation to external mass transfer coefficients. The effect of oscillation on mass transfer to drops is measured for three systems and the relationship between oscillation and internal circulation is considered. Finally, a technique is presented for measuring the effect of internal circulation in a drop, and a method of using this information to predict the increase in mass transfer rate that would result from the existence of internal circulation.

# EXPERIMENTAL

## A. EQUIPMENT AND PROCEDURES

### 1. Wind Tunnel for Internal Coefficients

#### a) Equipment.

The study of mass transfer from gas to liquid drops under conditions that will promote drop oscillation presents the following requirements:

(1) A sufficiently long contact time for absorption.

(2) A means of accurately controlling and measuring the drop size.

(3) A means of introducing the drop and removing it.

(4) A means of observing and recording the form of drops and their circulation.

In addition, the following characteristics are desirable:

(5) A flat velocity profile for the gas streams.

(6) Uniformity of the gas stream temperature and composition.

(7) Containment and conservation of the gas stream.

These requirements and characteristics can be provided by a closed loop system employing a wind tunnel. Such a system has been employed by Garner and Kendrick[16] for studies on unsupported drops. The system used in this study, to be described below, differs from Kendrick's primarily in the working section, having an orifice to provide a flat velocity profile, a hypodermic needle support in conjunction with a precision microburette to measure and support the drop, and a shield or sealing mechanism to isolate the drop from the gas stream during drop formation and drop removal.

Figure 1 is a diagram of the closed loop wind tunnel. Gas from a centrifugal blower (A) goes to a rotameter (B), the flow being controlled by a needle valve (C). The blower is a 300 Series Sawyer Bailey high efficiency miniature blower powered by a 15,000 R.P.M. motor and capable of delivering 20 C.F.M. air against a static pressure of 20 inches of water. A bypass line (D) with a screw clamp (E) leads back to the blower suction side. This serves to reduce vacuum and minimize leaks into the system. Cooling to the gas stream is provided in the bypass line by passing water through a three/sixteenths inch copper line (F).

The gas from the rotameter is expanded into the bottom of an 18 inch length of 1.75 inch aluminum tube (G) where its velocity is slowed down. Woven copper packing (H) helps to reduce any large eddies as well as equalize thermal conditions. The gas stream then emerges through an orifice (I) into the working section or box (J). The stream is a cylindrical jet with a flat velocity profile, as shown in Figure 2. The orifice is machined from one-eighth inch plate with a three-eighths inch hole being in the form of a suction flare of one-eighth inch radial curvature terminating in a sharp

| | |
|---|---|
| A | Centrifugal blower, 300 Series Sawyer Bailey 15,000 RPM high efficiency, miniature |
| B | Rotameter |
| C | Flow control needle valve |
| D | Bypass line |
| E | Screw clamp flow control on flexible connection |
| F | Cooling coil; 3/16 inch copper tubing, 4 feet long |
| G | Aluminum approach tube 1.75 inch diameter by 18 inches long |
| H | Woven copper packing |
| I | Orifice plate, 1/8 inch thick, 3/8 inch orifice, 1/8 inch radial curvature suction flare |
| J | Working section |
| K | Exit tube, 10 mm. I.D. |
| L | Return line |
| M | Mercury U-tube manometer |
| N | Mercury U-tube manometer |
| O | Mercury thermometer |
| P | Mercury thermometer |
| Q | $SO_2$ make-up rotameter |
| R | Make-up $SO_2$ flow control needle valve |
| S | Sealed box for blower |
| T | Traversing stand |
| U | Microburette |
| V | Flexible connections between blower assembly and loop |

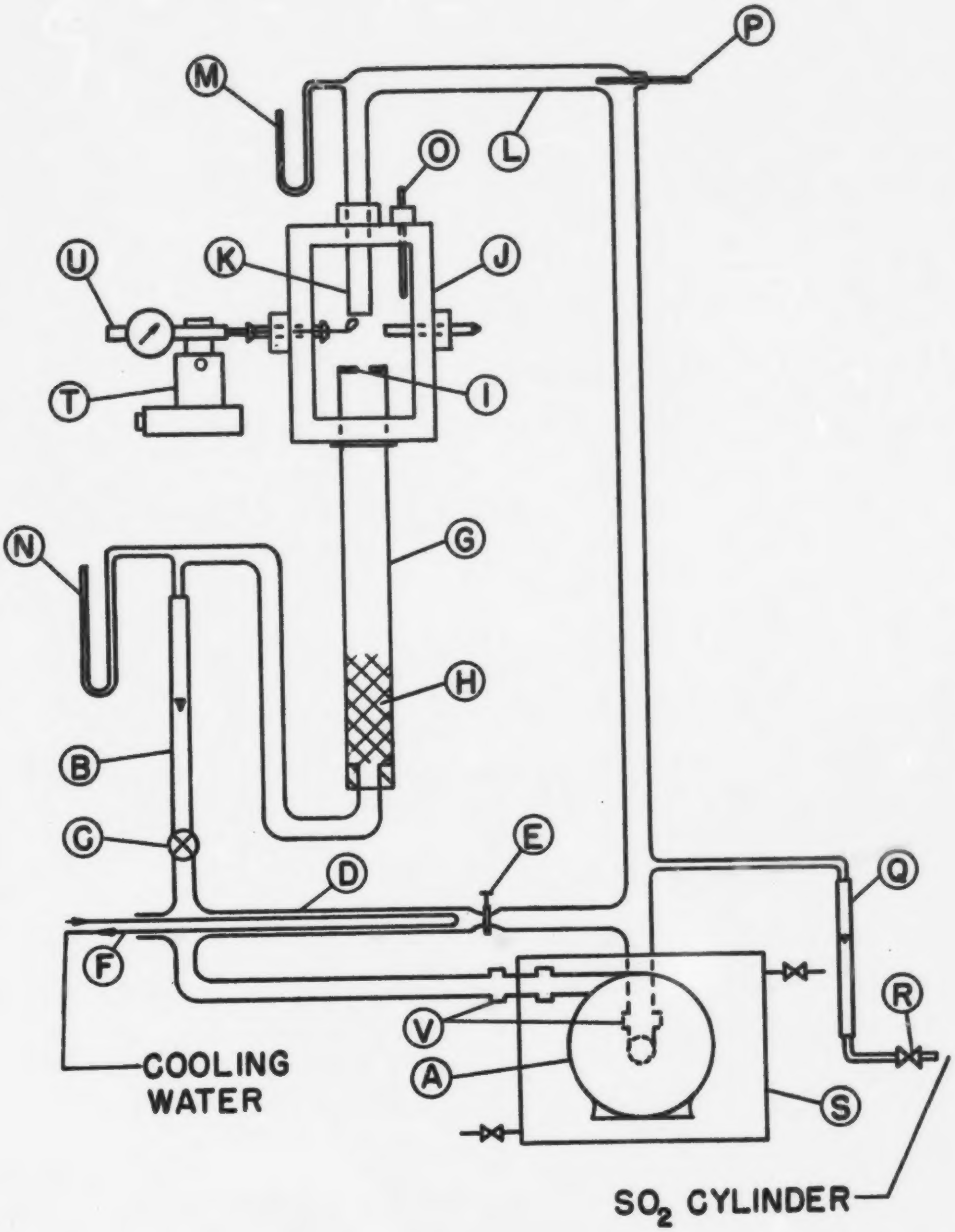


FIG. 1

WIND TUNNEL ASSEMBLY
FOR INTERNAL CIRCULATION STUDIES

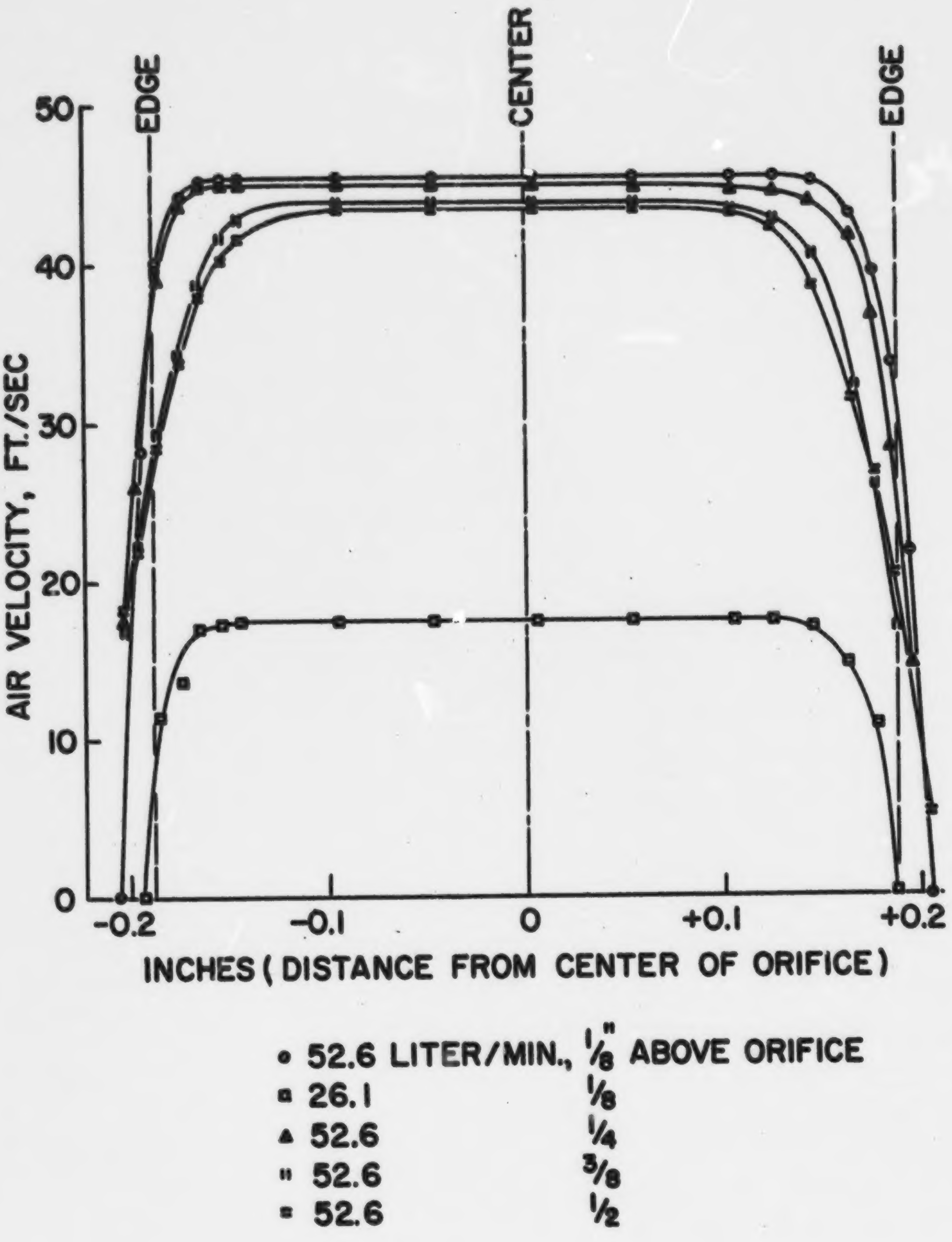


FIG. 2
ORIFICE VELOCITY PROFILE

edge downstream. The jet stream emerges from the working section through a 10 millimeter tube (K) and is returned via the return line (L) to the suction side of the blower. All lines, with the exception of short metal nipples at the blower and the needle valve consisted of one-inch glass tubing with smooth bends.

Fine mesh screens were employed in the aluminum tube and at the orifice in an attempt to control the level of turbulence and make it isotropic[16]. However, no difference could be noted when they were present and their use was abandoned when difficulties were encountered due to drops falling on them as was prone to occur periodically.

Pressures at the rotameter and the gas stream are measured by U-tube manometers (M) (N) filled with Meriam Oil. Temperatures are measured by mercury thermometers (O) (P) graduated in one degree Centigrade intervals.

A stream of make-up gas is metered through a rotameter (Q) and needle valve (R) at the suction side of the blower so as to insure that any gas leakage is out of rather than into the system. The blower is sealed in a metal box (S) which nullifies leakages that existed in the seals of the high speed blower. The blower assembly is connected to the rest of the system by flexible connections (V) so as to minimize transmission of any vibrations. All flexible connections and all joints were painted with lacquer to eliminate leaks.

The working section, or box, is shown in Figure 3, and is fabricated from one-eighth inch aluminum. Two sides consist of removable flat glass windows (A) for observation and distortion-free

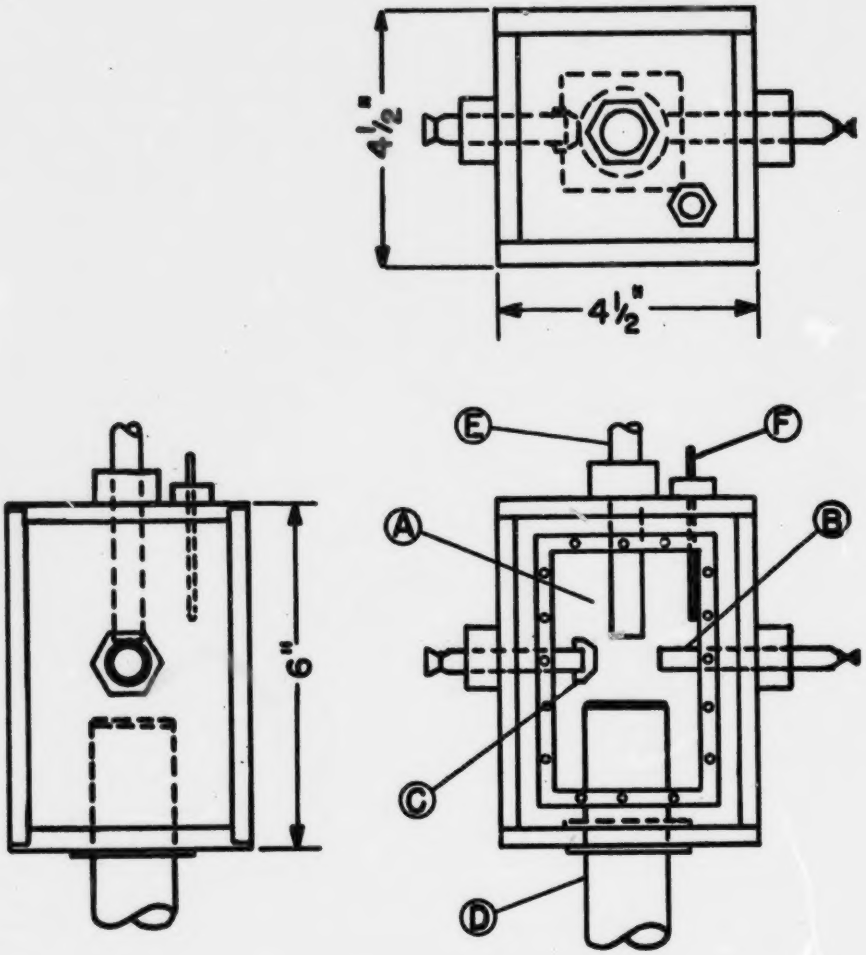


FIG. 3

WORKING SECTION

photography. All openings consist of packing glands with O-ring seals. A movable shield (B) consisting of 10 mm. tubing can be pressed against the rubber stop of the tube guide (C) and allow isolation of the drop from the gas stream during drop formation and drop removal.

The drop support assembly is shown in Figure 4 and consists of a special hypodermic tube, a microburette, a guide, and a traversing and supporting mechanism.

The hypodermic tubes consist of 15 gauge stainless tubing with a Luer base, the tubing telescoping to the desired diameter. The tube has a sealed end and is provided with a hole drilled perpendicular to the centerline of the tube approximately 1.5 mm. from the end. Total tube length is three and one-half inches. Three tube sizes were used, their outside diameters being 0.017 inches, 0.028 inches, and 0.037 inches. The drilled holes were 0.006 inches, 0.012 inches, and 0.020 inches, respectively. A tube guide sealed to the needle helped insertion into and removal from the working chamber.

The microburette was specially fabricated by Nuclear, Ohio, and has a working capacity of one-tenth of a milliliter. It is equipped with a two-inch dial indicator directly connected to the plunger as in a depth gauge, the dial having 100 subdivisions in one complete revolution; each revolution is equal to 0.001 milliliter, and each subdivision represents 0.0001 milliliter. The volume can be read to 0.00005 milliliters with no difficulty.

A. Traversing stand

B Forward traversing block

C. Forward traversing screw

D. Lateral traversing block with recess for microburette

E. Lateral traversing screw

F. Nuclear, Ohio, Microburette, 0.1 cm.$^3$ capacity, dial subdivided into 100 units, each revolution equals 0.010 cm.$^3$

G. Tube guide, sealed to hypodermic tubing

H. O-ring to seal guide to box inlet

I. Hypodermic support element

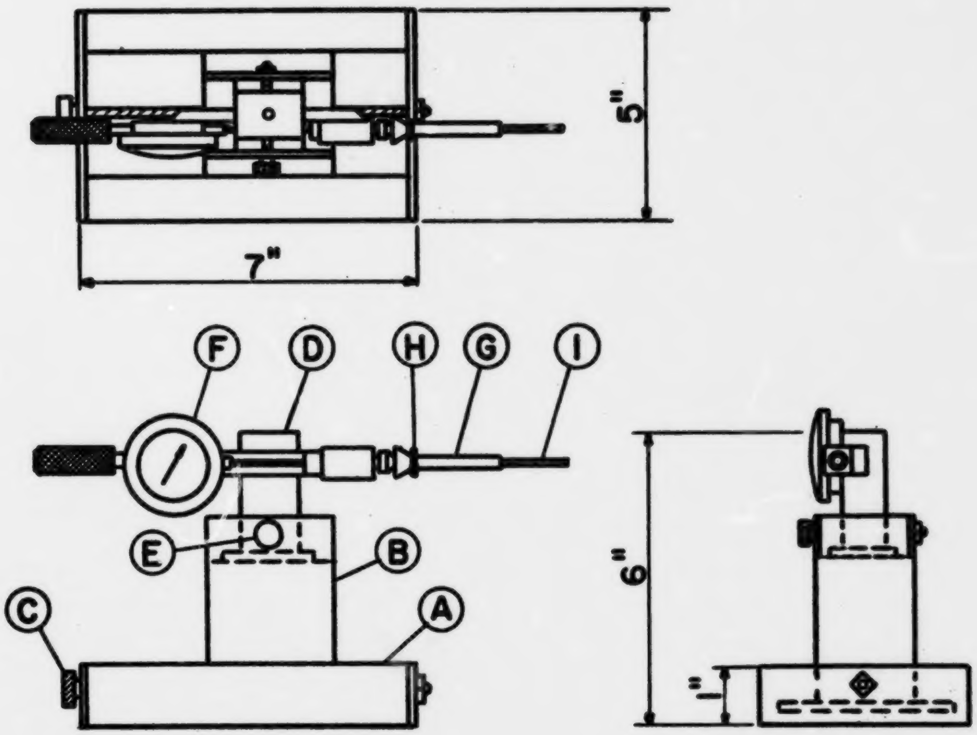


FIG. 4
DROP SUPPORT ASSEMBLY

The traversing support stand was fabricated out of brass and allowed fine traverse adjustment sideways and forward, as well as rapid forward movement. This allowed accurate positioning of the drop and ready insertion and removal.

The entire wind tunnel assembly is housed in a walk-around hood.

### b) Procedure

The system and blower box were purged with $SO_2$ gas until a gas analysis by absorption in hydrogen peroxide solution in a Burrell Gas Analyzer indicated a composition greater than 95% $SO_2$. The microburette was filled with the absorbing liquid, and the system and the full microburette were allowed to come to ambient temperature. The air flow was preadjusted to the desired value. A drop was formed outside the box in air and then positioned in the air-filled shield tube inside the working chamber. The shield could then be removed and the blower started, or the converse. The former method was more satisfactory. At the end of the exposure, the above procedure would be repeated in reverse, the drop then being rapidly withdrawn and plunged into a measured quantity of hydrogen peroxide solution for analysis. With practice, dexterity was developed to the point where transfer time of the drop consistently amounted to approximately two seconds. No correction was made for this time. The actual exposure time in the chamber was measured by a stopwatch. At the end of every eight runs, or more frequently, the gas stream was re-analyzed to establish that air leaks had not diluted the $SO_2$.

### c) Analysis

The $SO_2$ absorbed was determined by measuring the conductance of a known quantity of 0.003 molar solution of hydrogen peroxide used to oxidize the $SO_2$ to sulfuric acid[1]. An Industrial Instruments Model RC 16B2 Conductivity Bridge having a range of 0.2 to 2,500,000 ohms and bridge current frequencies of 50-60 cycles per second or 1000 cycles per second was used in conjunction with a conductance cell having platinized platinum plate electrodes, with a cell constant of approximately 0.1 $cm.^{-1}$. A curve was established experimentally relating the specific conductance to the concentration of $H_2SO_4$. The curve was found to be in good agreement with literature values[34].

### d) Motion Cinematography

The oscillatory motion of drops with an air stream blowing by them was studied by means of motion pictures. The circulation velocity within these drops was also determined for these pictures by measuring the travel of fine aluminum particles suspended in the drops. Water drops which exhibited high frequencies of oscillation and rapid velocities required the use of a 16mm Fastax High Speed Motion Picture Camera equipped with a 50mm f/2 Fastax-Raptar Wollensak lens with appropriate extension tubes. The camera was operated at speeds of 400-1200 frames per second by varying the voltage to the camera. Lighting was provided by a GE Photoflood Lamp RFL-2. Kodak Tri-X Negative film was used.

The glycols and glycerine which exhibited lower frequencies and slower velocities were photographed by a 16mm Paillard-Bolex motion picture camera operated at 64 frames per second with the shutter 1/4 open, giving individual frame exposures of approximately 1/500 second. Kodak Plus-X Reversal Type film was used.

An auxilliary means of observing the drops during a run consisted of projection of the drop image by a 100 watt projection light through a 20 power wide field tube microscope on a 8 by 10 inch ground glass screen. A graticule subdivided in thousandths of an inch was an integral part of this projection system.

### 2. Wind Tunnel for External Coefficients

The effect of oscillatory motion of a sphere on the outside coefficient can very conveniently be measured by vibrating a solid sphere of pure material subliming into the gas stream. Naphthalene serves this purpose admirably, and has been used in the celebrated studies of Frossling[14] and those of Christian and Kezios[5].

Figure 5 is a diagram of the wind tunnel and vibration assembly used. Dry air is metered through a 1 - 15 C.F.M. Fisher and Porter Rotameter (B) with a needle valve control (A) and passes through a heating chamber (C) which contains a 250 ohm resistance heating wire (D). The heat input is regulated by a Variac (E). The heated air is introduced into the wind tunnel (F) which consists of a 16 inch long by 1.91 inch diameter Pyrex tube necking down to a smooth nozzle 0.78 inches in diameter. This nozzle provides a flat velocity profile within 1/16 inch from the edge at a level of 5/16

| | |
|---|---|
| A | Air flow control needle valve |
| B | 1-15 C.F.M. rotameter |
| C | Heating chamber 16" long X 1.75" O.D. tube |
| D | 250 ohm resistance heating wire |
| E | Variac for heater |
| F | Wind tunnel, Pyrex tube 16" long X 1.91" O.D., nozzle 0.78" I.D. |
| G | Copper wire mesh for temperature and velocity stability |
| H | Naphthalene sphere |
| I | Sphere vibration assembly consisting of 1/10 HP variable speed motor, eccentric cam, and spring loaded sphere support and guide |
| J | 0-100°C thermometer |
| K | Mercury manometer |

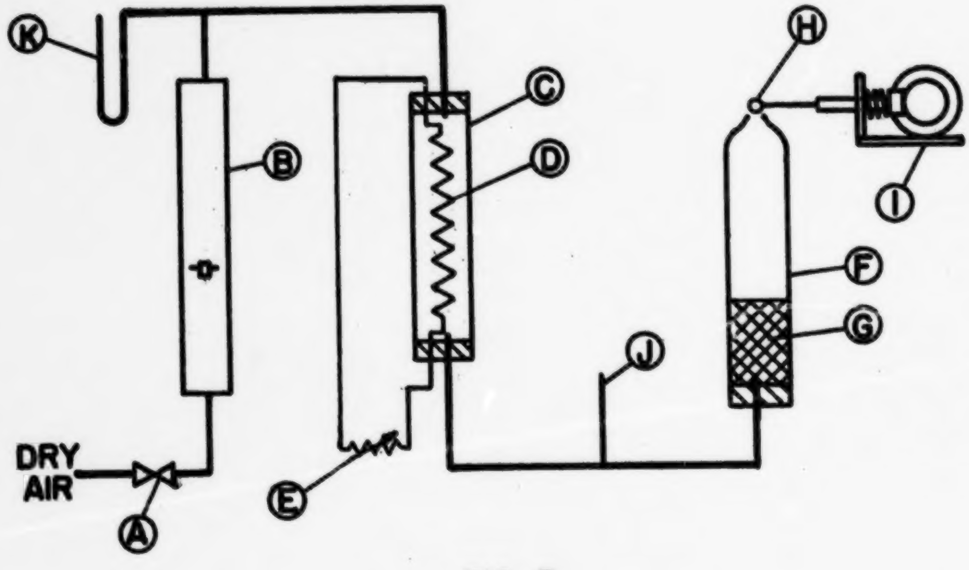


FIG. 5

WIND TUNNEL ASSEMBLY FOR OUTSIDE COEFFICIENT STUDIES inches above the orifice, and within 1/32 inch from the edge at 1/2 inch above the orifice. The bottom part of the wind tunnel is packed with copper mesh (G) for temperature and velocity stability. Temperature and pressure are measured by a mercury thermometer (J) and a U-tube manometer (K) filled with mercury. The temperature at the location of the sphere was within a fraction of a degree of the temperature indicated by the thermometer (J).

The naphthalene sphere (H) is supported by a steel wire imbedded into it and attached to the piston of the vibration assembly (I), which is shown in detail in Figure 6. The assembly was capable of imparting a frequency of vibration of 10-75 c.p.s. with an amplitude of 1/4 inch. However, attempts to vibrate the sphere at frequencies much above 20 c.p.s. generally resulted in disintegration of the sphere.

The naphthalene spheres were formed by pouring molten naphthalene into a mold containing the support wire. The mold was made from dental plaster, sealed with epoxy resin to eliminate pores, and wiped with a thin film of silicone fluid to facilitate release. The silicone appears to have no effect on the naphthalene surface[5]. Molds of varying sizes were used.

The amount of material sublimed was determined by weighing the sphere on an analytical balance before and after exposure. Sphere diameter was measured by a micrometer. Exposure was timed by a stopwatch.

(A) Variable resistance to control motor speed

(B) 110V. stirrer motor (2250 R.P.M. max.)

(C) Eccentric cam., 1/4 inch eccentricity

(D) Piston

(E) Spring

(F) Bearing block

(G) Set screw

(H) Support wire

(I) Naphthalene sphere

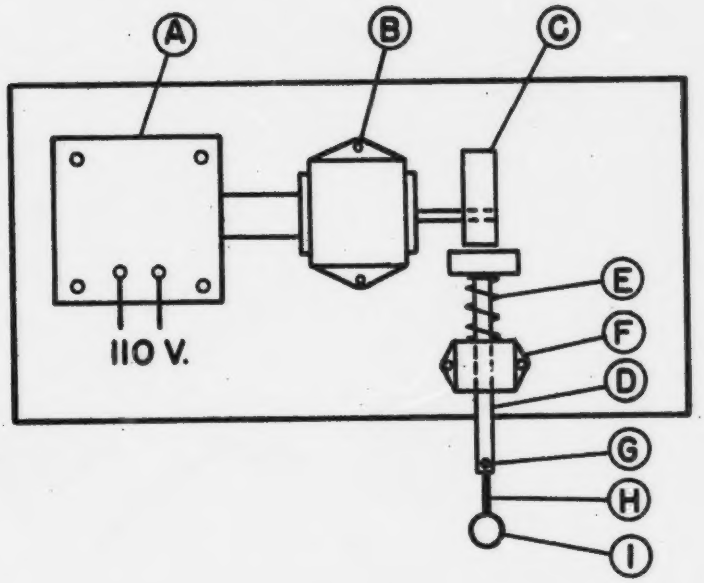


FIG. 6

VIBRATION ASSEMBLY

### 3. Controlled Forced Circulation Through a Drop

One means of creating a controlled amount of circulation in a drop is to suspend a drop from the tip of two concentric tubes and force fresh liquid into the drop through the central tube, withdrawing liquid through the annulus.

Initial attempts to construct an apparatus to do this were concentrated on a specially constructed high precision double displacement pump, using a common piston to force liquid from one side of the pump into the drop, while withdrawing liquid from the other side. This unit was abandoned after many efforts and modifications failed to give satisfactory operation.

A second all-glass system was constructed, eliminating the mechanically moving parts and relying on displacement by density difference. This is shown in Figure 7. Mercury from reservoir (C) is allowed to run into reservoir (E) which contains the liquid to be exposed. The liquid is displaced through the rotameter (F), at a rate controlled by needle valve (G) through the center tube of the drop assembly (I) into the drop (K). As the liquid is forced into the drop, an equal amount is withdrawn through the drop assembly annulus back to the mercury reservoir (C) to take the place of the mercury that has left. $SO_2$ gas is replaced in the contact chamber (J) as it is absorbed by a syringe reservoir (M) whose plunger is advanced manually at a rate necessary to maintain the system pressure as indicated by the U-tube manometer (L). A Gilmont Microburette (H) is used to adjust the drop to the desired size.

A Mercury load reservoir, 125 cm.$^3$

B Outlet for removing exposed liquid

C Upper reservoir for mercury feed and exposed liquid accumulation 1.8" O.D. x 4" long, 130 cm.$^3$

D Liquid load reservoir, 125 cm.$^3$

E Bottom reservoir for mercury accumulation and liquid feed 1.8" O.D. x 6" long, 200 cm.$^3$

F Liquid feed rotameter, F and P. No. 05-15 tube with special glass float for $H_2O$, No. 4 Brooks with tantalum float for propylene glycol

G Hoke 8 degree taper needle valve

H 0.1 ml. Gilmont Microburette

I Drop support assembly

J Contact chamber, 10 cm.$^3$

K Liquid drop

L Mercury manometer

M Gas reservoir, 50 cm.$^3$ syringe

N Gas surge chamber, 125 cm.$^3$

O Gas absorber, 125 cm.$^3$ flask with caustic solution

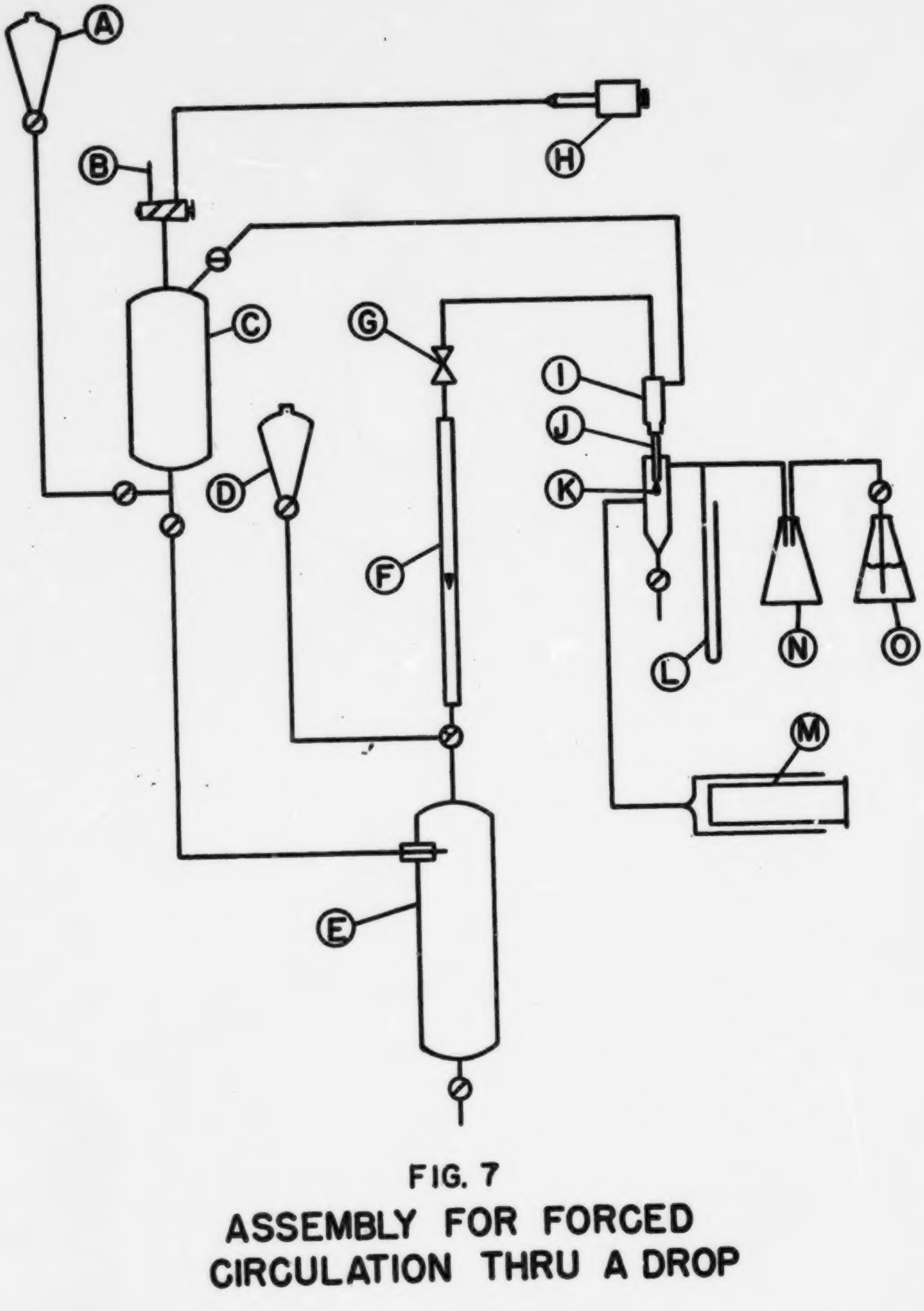


FIG. 7
ASSEMBLY FOR FORCED CIRCULATION THRU A DROP

## B. MATERIALS

1. Sulfur Dioxide: anhydrous grade $SO_2$ obtained from Matheson Co., Inc., with a minimum purity of 99.7% $SO_2$.

2. Glycerine: Mallincrodt Analytical Reagent, meets A.C.S. specifications. Minimum assay 95% by volume. The physical properties of the lot used indicated a glycerol content of about 97%.

3. Propane diol (1-2): Matheson Coleman and Bell, Boiling Point 186-187°C. Properties of the lot used indicated a purity greater than 98%.

4. Ethylene Glycol: Matheson Coleman and Bell, Boiling Point 195-197°C. Properties of the lot used indicated a purity greater than 98%.

5. Naphthalene: Baker Analyzed Reagent, Crystal, Melting Point 79-81°C.

## C. PHYSICAL PROPERTIES

### 1. Solubility at $SO_2$

The solubility of $SO_2$ in glycerine, propylene glycol, and ethylene glycol were determined at 25, 30, and 40 degrees Centigrade by bubbling $SO_2$ gas through the liquid in a constant temperature bath for a period in excess of 12 hours until a constant value was obtained indicating saturation. Aliquots of the saturated solution were measured by the microburette into peroxide solution for conductance measurements. The results are presented in Figure 8. At least two runs were made at each temperature for all except two points. The solubility of $SO_2$ in $H_2O$ was taken from literature[26] and has also been plotted on Figure 8.

### 2. Viscosities

An Ostwald type tube viscometer in a thermostat was used to measure the viscosities of the glycerine and glycol solutions containing varying amounts of $SO_2$ Table 1 represents values from smoothed curves obtained from cross-plots of the data.

### 3. Densities

Conventional bulk pycnometers of approximately 5 milliliter capacity were used to determine densities of the glycerine and glycol-$SO_2$ solutions. The pycnometers were calibrated with mercury and weighings were made on an analytical balance. A thermostat was used. Table 2 represents values from smoothed curves obtained by cross-plots of the data.

### 4. Diffusivities

An attempt was made to determine the diffusivity of $SO_2$ in the glycerine and glycol systems. The technique consisted of exposing an inverted glass tube filled with the solvent in a chamber full of $SO_2$. The tube functioned as a semi-infinite medium. After exposure of the desired time, the tube was removed and plunged into a hydrogen peroxide solution, oxidizing the $SO_2$ to $H_2SO_4$, determining the amount absorbed by measuring the conductance of the oxidized solution.

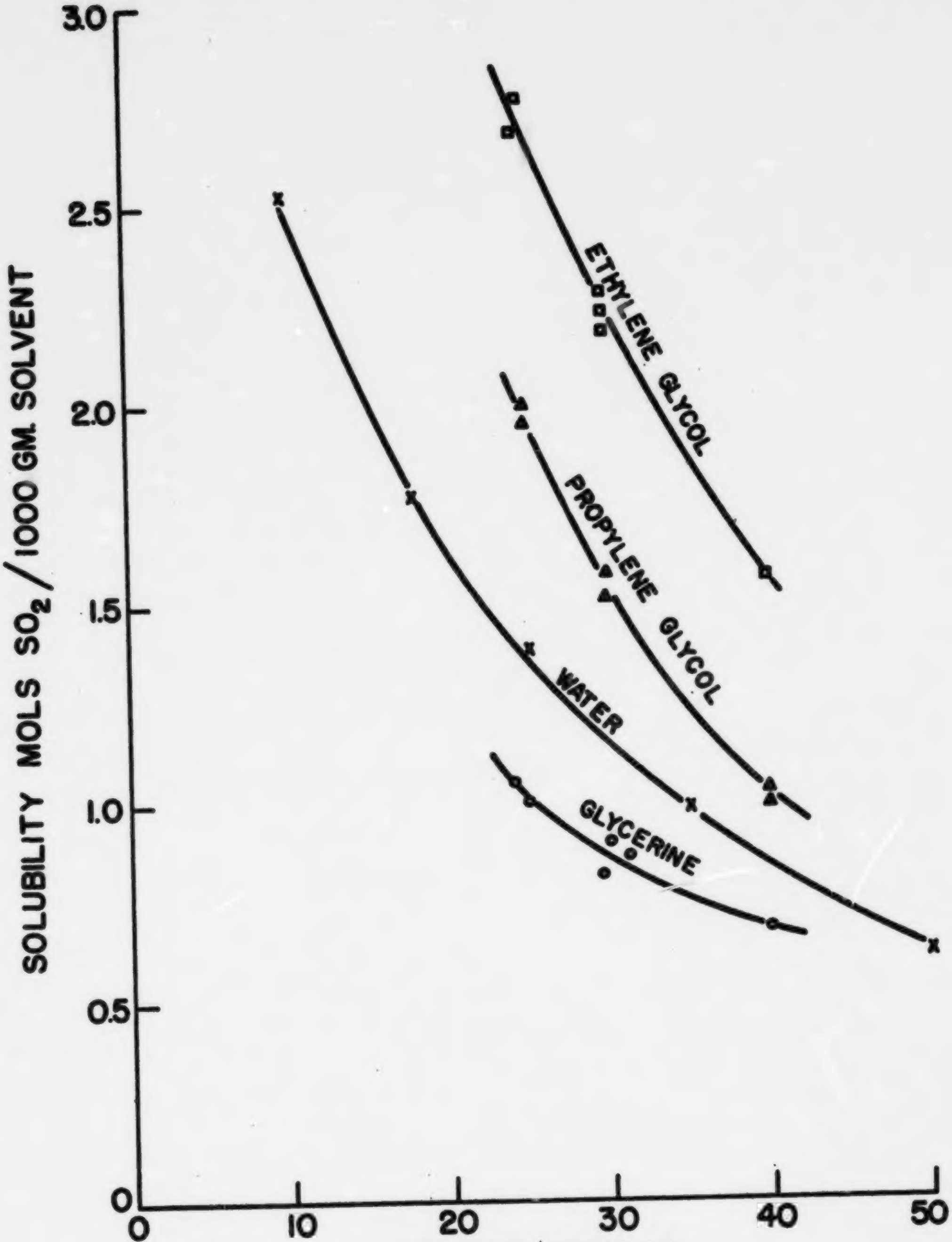


FIG. 8

SOLUBILITY OF $SO_2$

### TABLE 1

### VISCOSITIES OF SOLUTIONS CONTAINING $SO_2$ (SELECTED VALUES FROM CROSS-PLOTS OF SMOOTHED DATA)

| Concentration | Viscosity, csks. | | | |
|---|---|---|---|---|
| mols. $SO_2$/liter soln. | 20°C | 25° | 30° | 40° |
| GLYCERINE-$SO_2$ SYSTEM | | | | |
| 0 | 575 | 354 | 228 | 122 |
| 0.25 | 485 | 307 | 193 | 92 |
| 0.50 | 425 | 268 | 165 | 70 |
| 0.75 | 375 | 230 | 142 | 54 |
| 1.0 | 335 | 201 | 122 | ... |
| ETHYLENE GLYCOL-$SO_2$ | | | | |
| 0 | 19.0 | 15.6 | 13.8 | 8.8 |
| 0.50 | 16.5 | 13.7 | 11.2 | 7.7 |
| 1.0 | 14.5 | 12.0 | 9.8 | 6.7 |
| 1.5 | 13.0 | 10.6 | 8.7 | 5.8 |
| 2.0 | 11.3 | 9.3 | 7.6 | ... |
| 2.5 | 10.0 | 8.1 | .... | ... |
| PROPYLENE GLYCOL-$SO_2$ | | | | |
| 0 | 55.0 | 44.0 | 34.5 | 21.5 |
| 0.50 | 46.0 | 34.0 | 25.0 | 13.7 |
| 1.0 | 35.0 | 25.0 | 18.0 | 9.0 |
| 1.5 | 26.0 | 18.5 | 13.2 | .... |
| 1.9 | 21.0 | 14.0 | .... | .... |

## TABLE 2

## DENSITIES OF SOLUTIONS CONTAINING $SO_2$ (SELECTED VALUES FROM CROSS-PLOTS OF SMOOTHED DATA)

| Concentration | Density, gm./cm.$^3$ | | | |
|---|---|---|---|---|
| mols. $SO_2$/liter soln. | 20°C | 25° | 30° | 40° |
| **GLYCERINE-$SO_2$** | | | | |
| 0 | 1.253 | 1.249 | 1.246 | 1.241 |
| 0.25 | 1.257 | 1.254 | 1.250 | 1.245 |
| 0.50 | 1.261 | 1.258 | 1.255 | 1.249 |
| 0.75 | 1.265 | 1.262 | 1.259 | 1.252 |
| 1.00 | 1.269 | 1.266 | 1.263 | . . . |
| 1.20 | 1.272 | 1.269 | . . . | . . . |
| **PROPYLENE GLYCOL-$SO_2$** | | | | |
| 0 | 1.037 | 1.034 | 1.030 | 1.024 |
| 0.50 | 1.053 | 1.049 | 1.045 | 1.038 |
| 1.00 | 1.068 | 1.064 | 1.060 | 1.052 |
| 1.50 | 1.083 | 1.079 | 1.075 | . . . |
| 1.90 | 1.096 | 1.092 | . . . | . . . |
| **ETHYLENE GLYCOL-$SO_2$** | | | | |
| 0 | 1.112 | 1.109 | 1.106 | 1.100 |
| 0.50 | 1.123 | 1.120 | 1.116 | 1.111 |
| 1.00 | 1.134 | 1.130 | 1.126 | 1.122 |
| 1.50 | 1.145 | 1.140 | 1.137 | 1.133 |
| 2.00 | 1.155 | 1.151 | 1.147 | . . . |
| 2.50 | 1.165 | 1.161 | . . . | . . . |

Knowing the amount absorbed, the time, and the flat surface area exposed, one can calculate an average diffusivity coefficient.

The inverted tube was used as a means to avoid convection currents caused by the increased density of the solution as it absorbs $SO_2$.

The experimental results were erratic and much higher than what would be expected, being in the order of 4 to 13 times the values theoretically calculated. A possible explanation may be that convection currents may have existed by virtue of the large heat effects, and the poor thermal conductivity of the thick glass walls. This would allow a large temperature rise and associated density decrease of the concentrated solution, perhaps enough to cause it to rise in the tube, creating convection currents.

The diffusivity values used in this study were calculated by the method of Wilke and Chang[38], using the experimentally measured viscosities for glycerine and the glycol systems, and are presented in Figures 9, 10, and 11. Diffusivities calculated for the system $SO_2$-$H_2O$ using the viscosity of pure water appear in Figure 12 and compare well with experimental values.

### 5. Heats of Solution

Heats of solution were measured by bubbling $SO_2$ through the liquids in a 20 ml. Dewar calorimeter and noting the temperature rise on a thermometer graduated in 0.1°C increments. The heat equivalent and heat losses of the calorimeter were determined by measuring the power input to a nichrome heater in the calorimeter

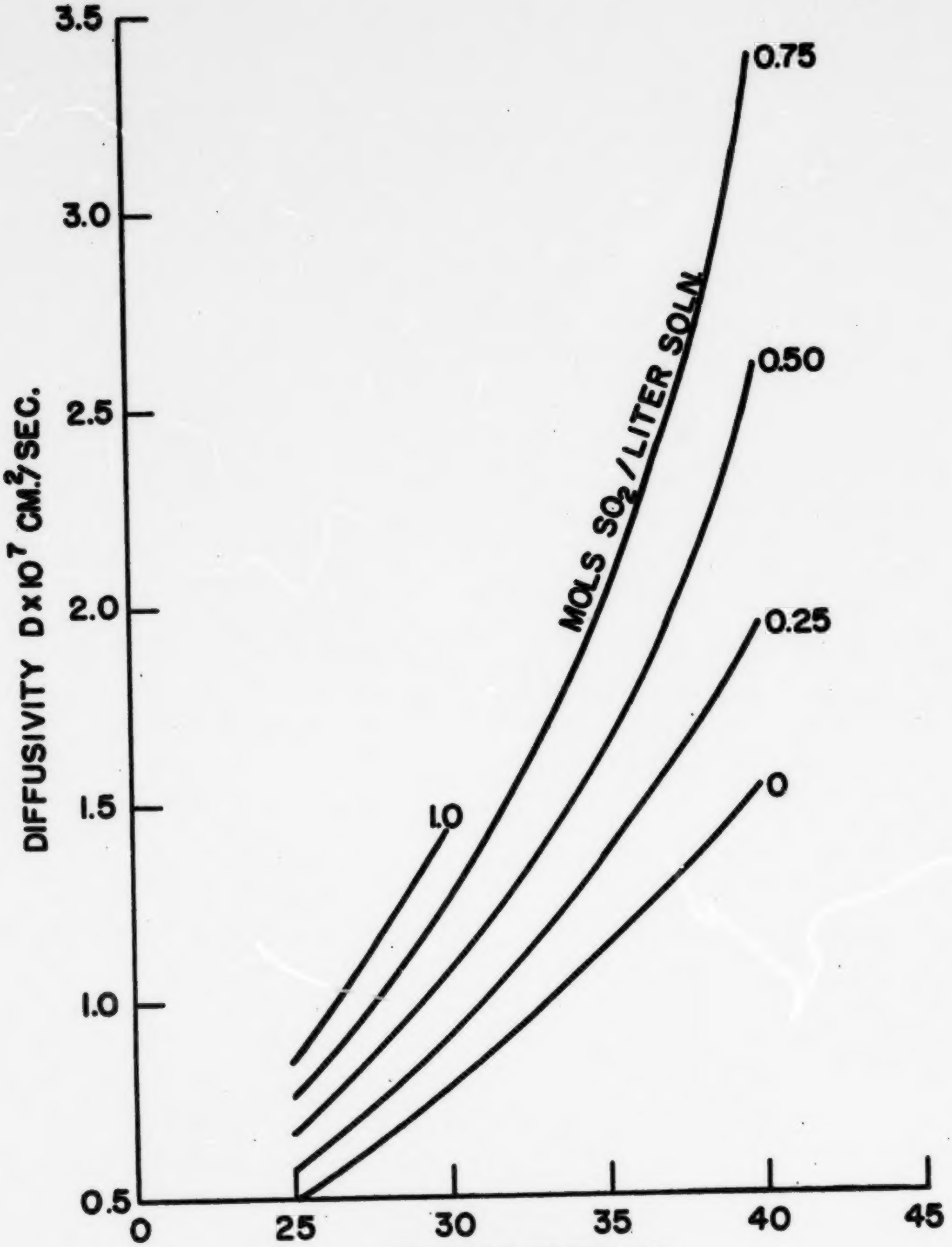


FIG. 9

THEORETICAL DIFFUSIVITY $SO_2$ IN GLYCEROL

# THEORETICAL DIFFUSIVITY
# $SO_2$ IN PROPYLENE GLYCOL

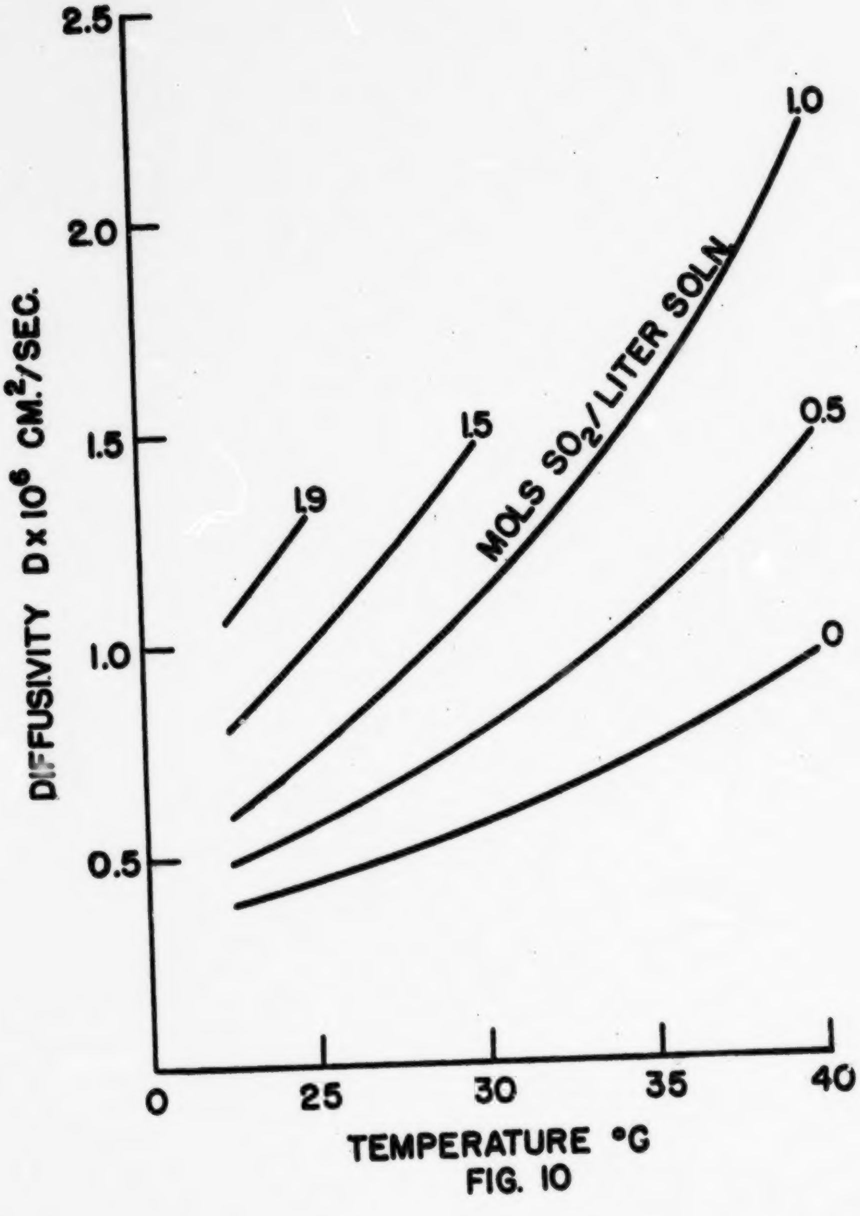


FIG. 10

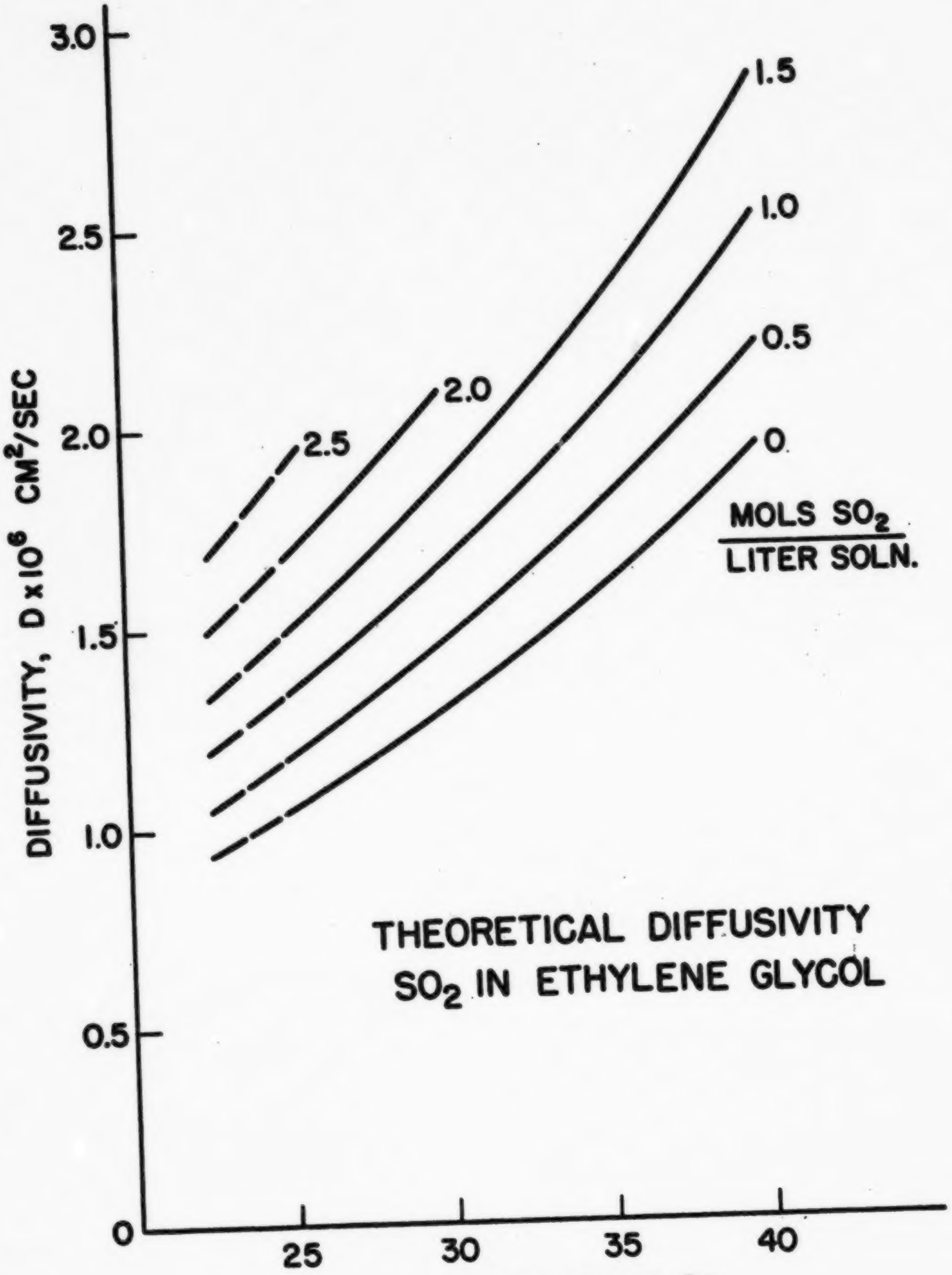

3.0
2.5
2.0
1.5
1.0
0.5
0
DIFFUSIVITY, D x 10⁶ CM²/SEC
1.5
1.0
0.5
0
2.0
2.5
MOLS SO₂ / LITER SOLN.
THEORETICAL DIFFUSIVITY
SO₂ IN ETHYLENE GLYCOL
25
30
35
40
TEMPERATURE °C

FIG. 11

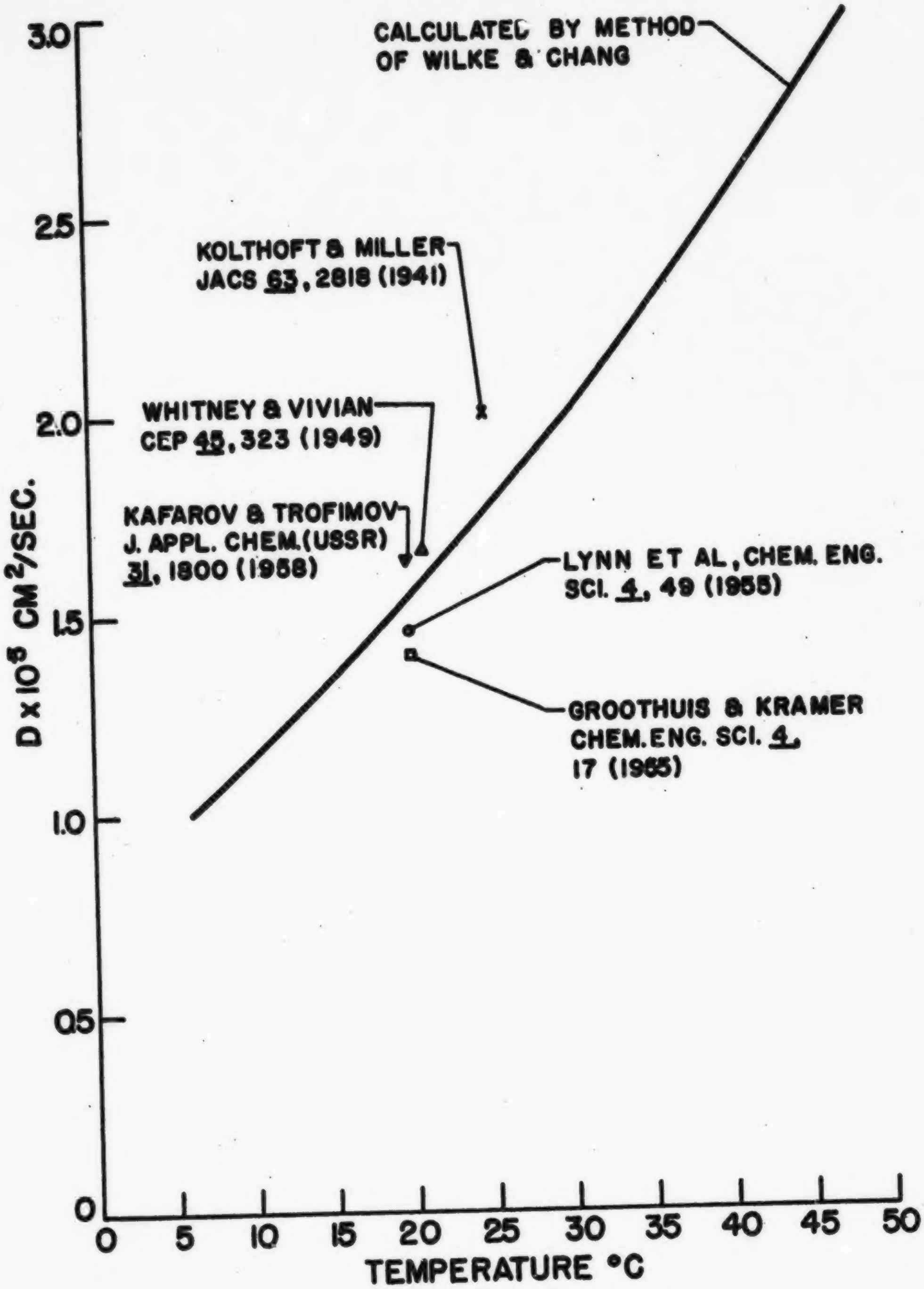


FIG. 12

DIFFUSIVITY OF $SO_2$ IN $H_2O$

under conditions identical to the experimental run. The results are presented in Table 3.

# TABLE 3

# HEATS OF SOLUTION FOR $SO_2$

| Run | Material | Mols $SO_2$ | $Q_{apparent}$ | $Q_{cal.}$ | $Q_{total}$ | ΔH cal./mol |
|---|---|---|---|---|---|---|
| ΔH-1 | Propylene Glycol | 0.0182 | 79.2 | 35.8 | 115.0 | 6320 |
| ΔH-2 | Propylene Glycol | 0.0189 | 80.6 | 35.7 | 116.3 | 6160 |
| | | | | | Avg. | 6240 $\frac{\text{cal.}}{\text{mol } SO_2}$ (±80) |
| ΔH-3 | Ethylene Glycol | 0.0191 | 92.7 | 32.7 | 125.4 | 6570 |
| ΔH-4 | Ethylene Glycol | 0.0182 | 83.7 | 31.5 | 115.2 | 6340 |
| | | | | | Avg. | 6455 $\frac{\text{cal.}}{\text{mol } SO_2}$ (±115) |
| ΔH-5 | Glycerol | 0.0069 | 23.7 | 3.5 | 27.2 | 4000 |
| ΔH-6 | Glycerol | 0.0067 | 24.3 | 3.5 | 27.8 | 4150 |
| | | | | | Avg. | 4075 $\frac{\text{cal.}}{\text{mol } SO_2}$ (±75) |

# RESULTS AND CONCLUSIONS

## A. OUTSIDE COEFFICIENTS

The effect of vibration on outside coefficients is demonstrated by comparing the experimental coefficients with the theoretically calculated ones.

The experimental coefficients were calculated from data on the average rates of naphthalene subliming into air at 50°C by means of the steady state relationship:

$$N_A = k_g(p_i - p_g) \tag{1}$$

where $N_A$ = rate of transfer, lb. mols/hr. ft.$^2$, $p_i$ = interfacial vapor pressure of naphthalene, atm., and $p_g$ = bulk stream vapor pressure of naphthalene, atm. = 0, and $k_g a$ = outside mass transfer coefficient, lb. mols/hr. ft.$^2$ atm.

The empirical coefficients were calculated from Frossling's correlation[14]

$$\frac{k_c d}{D_v} = 2.0\left[1 + 0.276\, N_{Re}^{1/2} N_{sc}^{1/3}\right] \tag{2}$$

and

$$k_g = \frac{k_c}{RT} \tag{3}$$

where $k_c$ = transfer coefficient, ft./hr., R = universal gas constant $= 0.729 \frac{\text{ft.}^3\ \text{atm.}}{\text{lb./mol. }^\circ\text{K}}$, $k_g$ = transfer coefficient, d = sphere diameter, ft., $D_v$ = molecular diffusivity in vapor, ft.$^2$/hr., $N_{Re}$ = Reynolds Number, and $N_{Sc}$ = Schmidt Number.

The theoretical and experimental values are plotted in Figure 13. No significant difference can be detected between stagnant and vibrating spheres. The experimental data fits the theoretical curves satisfactorily.

Other studies support the results obtained for mass transfer to drops. Previous investigations on the effect of vibration on heat transfer[2, 28, 30, 36] indicate that vibration has no effect on heat transfer coefficient when the vibration velocity is less than the air flow velocity. It would be reasonable to expect a similar relationship for mass transfer. In the naphthalene experiments the maximum frequency was 20 c.p.s. with an amplitude of 1/4 inch, yielding a vibration velocity of 0.84 ft. per second. This is much lower than the lowest air flow of 5 ft. per second that was used.

In the case of oscillating liquid drops, the extremes observed were maxima of 75 c.p.s. and 1/16 inch amplitude, which would yield a vibration velocity of less than 1 ft. per second. Thus we would not expect any significant increase of outside coefficient by virtue of the oscillation when dealing with forced gas convection past drops at moderate or high velocities. Some effect would most likely be expected at very low velocities as has been indicated by Elzinga's work[12] on heat transfer from drops falling through a liquid medium.

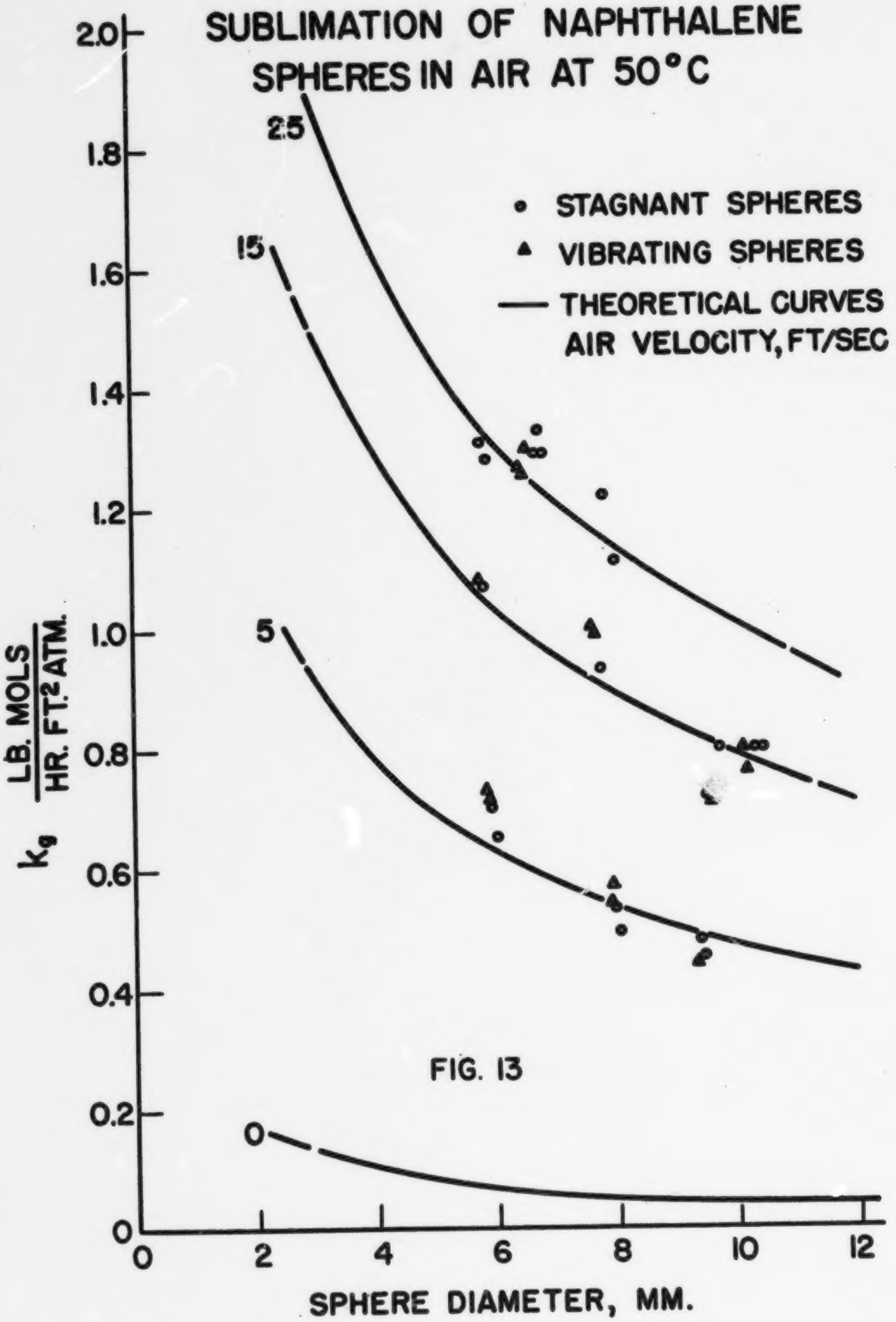

SUBLIMATION OF NAPHTHALENE SPHERES IN AIR AT 50°C
● STAGNANT SPHERES
▲ VIBRATING SPHERES
— THEORETICAL CURVES AIR VELOCITY, FT/SEC
25
15
5
0
$k_g$ $\frac{\text{LB. MOLS}}{\text{HR. FT.}^2\text{ ATM.}}$
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
SPHERE DIAMETER, MM.

FIG. 13

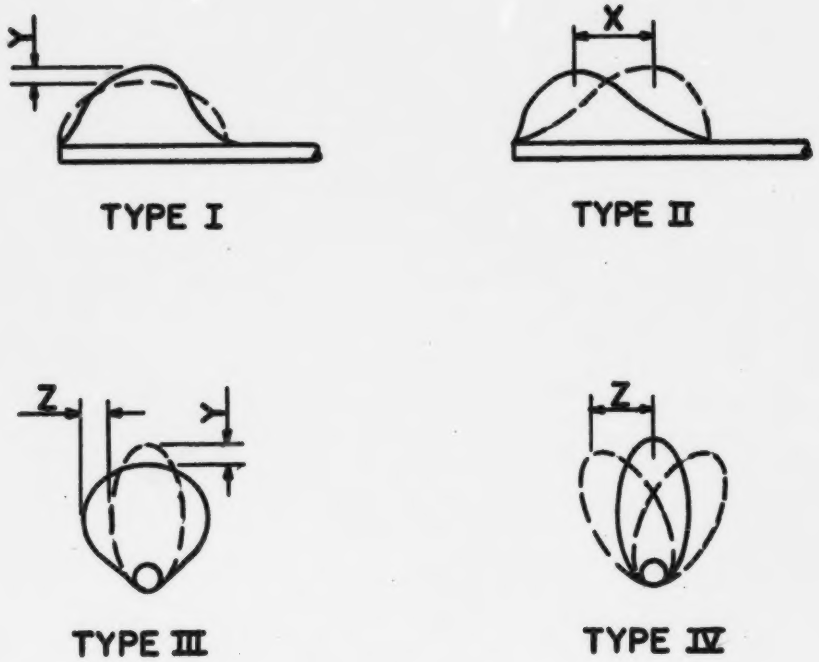
## B. INSIDE COEFFICIENTS

### 1. Oscillations of Drops

The nature of the oscillations observed falls into two categories which are depicted in Figure 14. Type I and II represent the view perpendicular to the support element which is considered the XY plane. Types III and IV represent the head-on view which is considered the YZ plane. Table 4 lists the values observed.

The first category of oscillation is one that may be considered a deformation, comparable to an oblate-to-prolate spheroid, and is that shown as Types I and III, while being listed as Y in Table 4. It is common to free-falling drops. The second category is one of displacement, and is shown as Types II and IV which are listed as X and Z, respectively, in Table 4. This type is unique to supported drops and would be expected to contribute significantly to an effect upon mass transfer.

Inspection of the movies showed the type and order of oscillations to be entirely random, as was the magnitude of oscillation amplitudes. The data reported in Table 4 represent maximum values observed, but not necessarily concurrent ones. It can be seen that the amplitudes are relatively small, increasing as the air velocity is increased. They are generally less than 10% of the drop diameter until blow-off velocities are approached, and then they increase to about 25%. The effect of drop size is not significant, but viscosity appears to play a more prominent role, decreasing the amplitudes as



TYPE I

TYPE II

TYPE III

TYPE IV

FIG. 14

TYPES OF DROP OSCILLATION

## TABLE 4

## AMPLITUDES OF OSCILLATION

| Material | Drop Diameter | Air Velocity | Amplitude, cm. | | |
|---|---|---|---|---|---|
| | cm. | ft./sec. | X | Y | Z |
| Propylene Glycol | 0.20 | 22.4 | . . . | 0.013 | 0.009 |
| | . . . . | 12.3 | n. | .011 | . . . |
| | . . . . | 7.1 | n. | .014 | n. |
| | 0.25 | 22.4 | 0.027 | .017 | .008 |
| | . . . . | 12.3 | n. | sl. | n. |
| | . . . . | 7.1 | n. | n. | n. |
| Ethylene Glycol | 0.20 | 22.4 | .024 | .042 | .057 |
| | . . . . | 12.3 | n. | .005 | .007 |
| | . . . . | 7.1 | n. | n. | n. |
| | 0.25 | 22.4 | .039 | .046 | .047 |
| | . . . . | 12.3 | . . . | .004 | .004 |
| | . . . . | 7.1 | n. | .005 | n. |
| Water | 0.20 | 24.5 | n. | .028 | . . . |
| | 0.25 | 18.2 | .011 | .008 | . . . |

**Note:**

n. = negligible, or less than 0.002 cm.
sl. = slight, or less than 0.004 cm.

viscosity increases. In the case of glycerine drops, the oscillations were too small to allow meaningful measurements.

Attempts to determine frequencies of oscillation from the motion pictures indicated the existence of two frequencies: those of the deformation type which were rapid, and those of the displacement type which were slower. In the case of $H_2O$, only the deformation type were noted. In the case of the glycols, both types were noted, but only the displacement type could be accurately measured at 64 frames per second. These data are shown in Table 5, and are compared to the frequencies of spheres oscillating between a prolate and an oblate spheroid calculated by the equation of Lamb[28] which is:

$$f = \left[\frac{8\sigma}{3\,m}\right]^{1/2} \qquad (6)$$

where $f$ = frequency of oscillation, $\sigma$ = surface tension, and $m$ = mass of sphere.

No satisfactory means were established to correlate the oscillation to the effective diffusivity.

## 2. Effective Diffusivities

Initial attempts to study the system $H_2O$-$SO_2$ were abandoned because of two difficulties:

a) The diffusivities were too large for use in this experimental technique, requiring short contact times and leading to large desorption losses in the transfer process.

b) Increases of a fraction of a degree in the gas stream temperature dropped the humidity below 100% causing significant evaporation of the drops.

## TABLE 5

## FREQUENCIES OF OSCILLATION

at 25°C

| Material | $a$ | $\sigma$ | $\rho$ | $f_t$ | Air Velocity | $f_a$ |
|---|---|---|---|---|---|---|
| | cm. | dynes/cm. | gm./cm.$^3$ | c.p.s. (Theory) | ft./sec. | c.p.s. (Actual) |
| $H_2O$ | 0.100 | 72.8 | 1.0 | 121 | 24.5 | 73 |
| | 0.125 | 72.8 | 1.0 | 87 | 18.2 | 75 |
| Ethylene Glycol | 0.100 | 48.0 | 1.11 | 94 | 22.4 | 23 |
| | 0.125 | 48.0 | 1.11 | 67 | 22.4 | 25 |
| Propylene Glycol | 0.100 | 72.0 | 1.03 | 119 | 22.4 | 27 |
| | 0.125 | 72.0 | 1.03 | 85 | 22.4 | 22 |
| Glycerine | 0.100 | 62.2 | 1.26 | 100 | 22.4 | 19 |
| | 0.125 | 62.2 | 1.26 | 72 | 22.4 | 22 |

Glycerine and the glycols have much smaller diffusivity coefficients and have negligible vapor pressures at the temperatures used and thus are well suited for this study. The solubility of $SO_2$ gas in these liquids is large enough to allow reliable analytical measurements on single drops.

For molecular diffusion into a sphere, the following differential equation describes[33] the change of concentration with time:

$$\frac{\partial c}{\partial t} = D\left[\frac{2}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2}\right] \tag{4}$$

where c = concentration, t = time, r = radius, and D = diffusivity. The solution of this equation[19] with appropriate boundary conditions leads to the expression for degree of saturation.

$$\left(\frac{c_s - c}{c_s - c_o}\right) = 1 - \left[\frac{6}{\pi^2}\sum_{n=1}^{0}\frac{1}{n^2}\exp\left(-\frac{Dn^2\pi^2 t}{a^2}\right)\right] = 1 - F \tag{5}$$

where F = fractional saturation, $c_s$ = saturated concentration, and $c_o$ = initial concentration.

This equation has been solved for values of F as a function of the dimensionless time group $\left(\frac{Dt}{a^2}\right)$ and may be found in graphical form in numerous places[7].

The experimental results have been correlated on the basis of degree of saturation versus the dimensionless time group. Although the oscillating drop is not a sphere, it was considered as having an effective radius equal to that of a sphere of equivalent volume. The justification of this is that it provides a convenient means of comparing the absorption of the drop to that of a rigid sphere.

The diffusivities used were calculated values based on a mean concentration. This mean was a numerical average of the initial and final average values of the surface and bulk concentrations. The location of the experimental curves relative to theory leads one to believe that the calculated diffusivities may be in error. However, this does not affect the comparison of oscillating drops to stagnant drops.

Thermal effects were calculated and shown to cause a temperature rise of 1-2 degrees in most cases. This temperature rise was neglected, since it could not be accurately measured, and since it could be shown that it did not alter the nature of the correlation.

The results are plotted in Figures 15, 16, and 17.

The system glycerine-$SO_2$ does not exhibit any significant difference between the stagnant and oscillating drops. A fairly large degree of scatter in the date undoubtedly contributes towards obscuring any small differences. The data are in good agreement with the theoretical curve.

It might be speculated that no large increases in absorption would be expected in such a highly viscous system that exhibits little or no internal circulation (velocities less than 0.2 cm/sec).

The system propylene glycol-$SO_2$ shows that there is a distinct difference between the stagnant and oscillating drops. The oscillating drops attain a given saturation 2-8 times as rapidly as the stagnant drops. This could be restated as exhibiting a greater "effective" diffusivity. The magnitude of the effective diffusivity appears to be dependent on the degree of saturation under

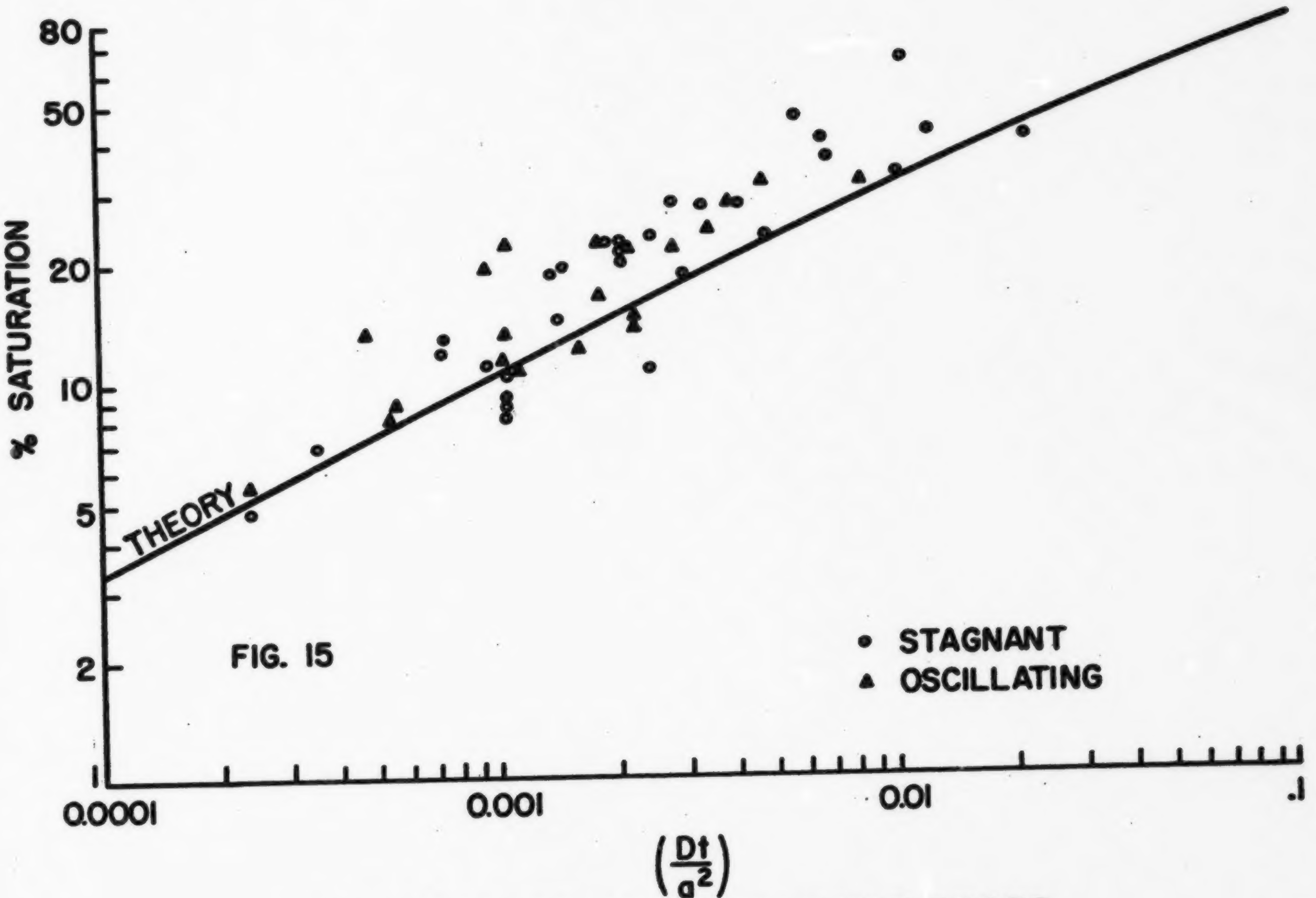


FIG. 15

ABSORPTION OF $SO_2$ BY GLYCERINE DROPS

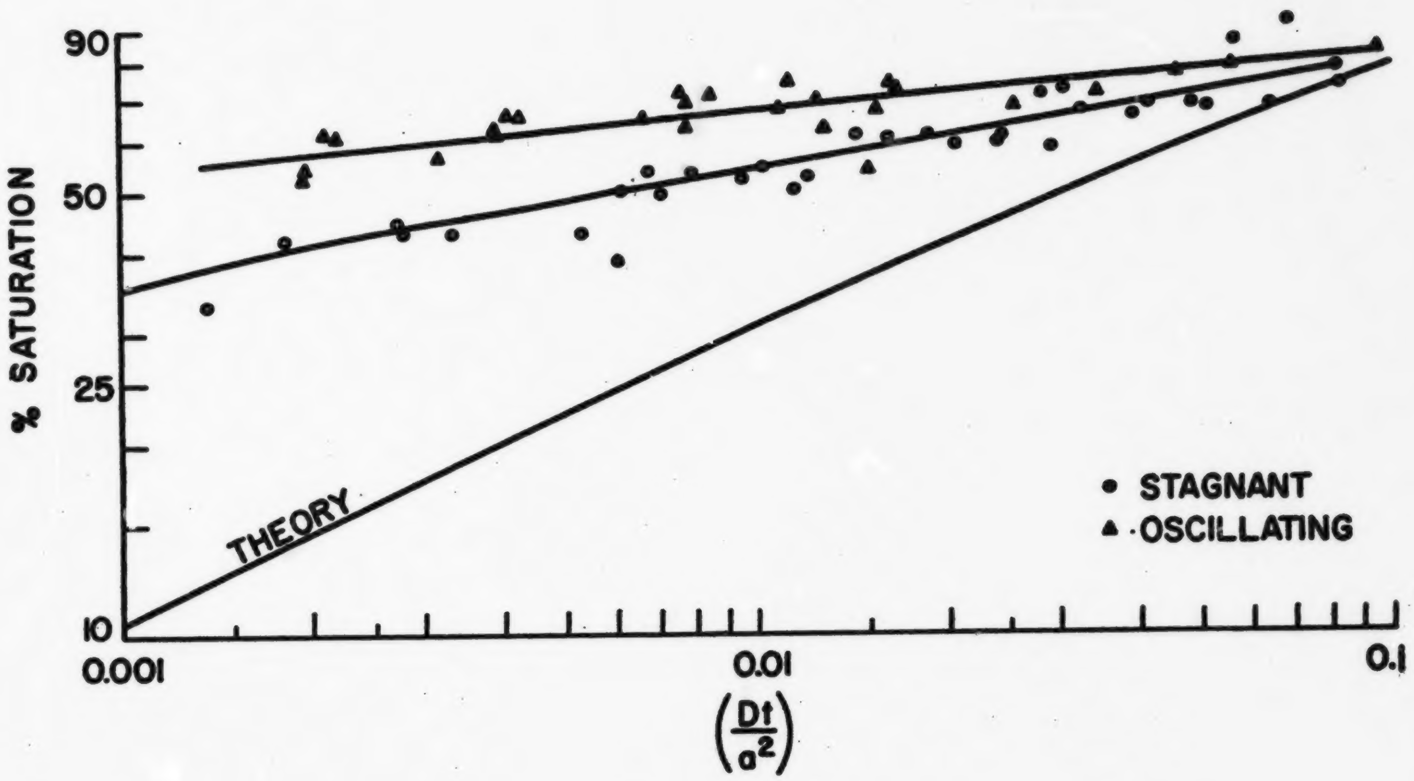


FIG. 16

ABSORPTION OF $SO_2$
BY PROPYLENE GLYCOL DROPS

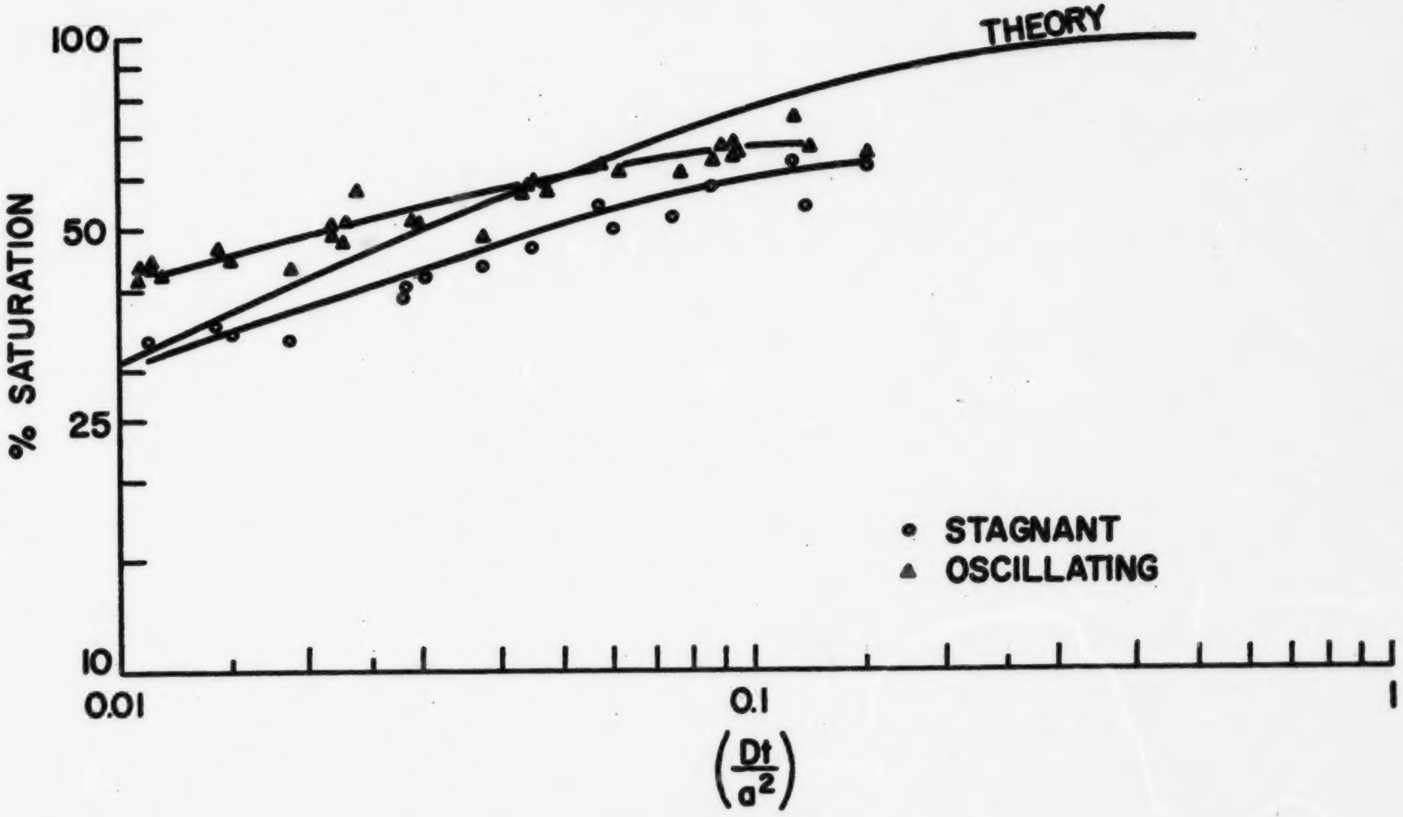


FIG. 17
ABSORPTION OF $SO_2$
BY ETHYLENE GLYCOL DROPS

consideration, being greatest at low saturations. This is contrary to the effect expected from subsequent studies on forced circulation which predicts higher values at the higher saturations.

All the data appears to be above the theoretical curve. Three possible explanations for this may be:

(1) the calculated diffusivities are lower than the true diffusivities,

(2) the "stagnant" drops actually exhibit a small amount of circulation as a result of density gradients, or

(3) the drop is sufficiently deformed so as to present thin sections at the point of contact with the support member so as to saturate more rapidly. This would be more pronounced for the oscillating drops.

Drop size over the range of 0.0042 to 0.0110 ml., $SO_2$ gas velocity over the range of 10.0 to 22.4 ft./sec., and support element diameters over the range of 0.017-0.037 inches were investigated. The 0.017 inch element was too small to support drops large enough to work with. No significant effect upon the effective diffusivity could be measured for these variables in the ranges studies.

The system ethylene glycol-$SO_2$ also shows an increased effective diffusivity for the oscillating drops equal to about 2.5 times the molecular diffusivity, and fairly constant with saturation. The magnitude of this increase in diffusivity is smaller than anticipated. The effects of varying gas velocity over the range of 10.0-22.4 ft/sec., support element diameter over the range of 0.028-0.037 inches, and drop diameters over the range of 0.0042-0.0082 ml. were investigated. The element variable shows no effect. Drop size shows a small effect on effective diffusivity, as can be seen in Figure 18. Increased gas velocity increases effective diffusivity as can be seen in Figure 19; this would be expected from consideration of dependency of internal circulation on gas velocity.

The above results show that oscillation of drops does indeed increase mass transfer rates, although to a smaller extent than anticipated. The mechanism appears to be predominantly one of internal circulation, augmented by deformation. What appears at first to be a discrepancy shows up as a greater effective diffusivity at lower saturations. On more careful consideration, one sees that this could be plausibly explained by the deformation of the drop. At the initial stage of absorption, most of the transfer is taking place near the surface, and would not be affected by internal circulation. Increased area due to thin sections, such as at the support element, would allow greater initial rates and thus would appear to give a high effective diffusivity. As these quickly saturate and transfer to the major part of the sphere takes over, internal circulation becomes of importance. Although internal curculation will have an effect on the rate, it could be smaller than that of the short duration effect of deformation. From the practical standpoint, the initial period is short, and the longer period as higher saturations are approached is the more important one. Thus, internal circulation would be the more important factor.

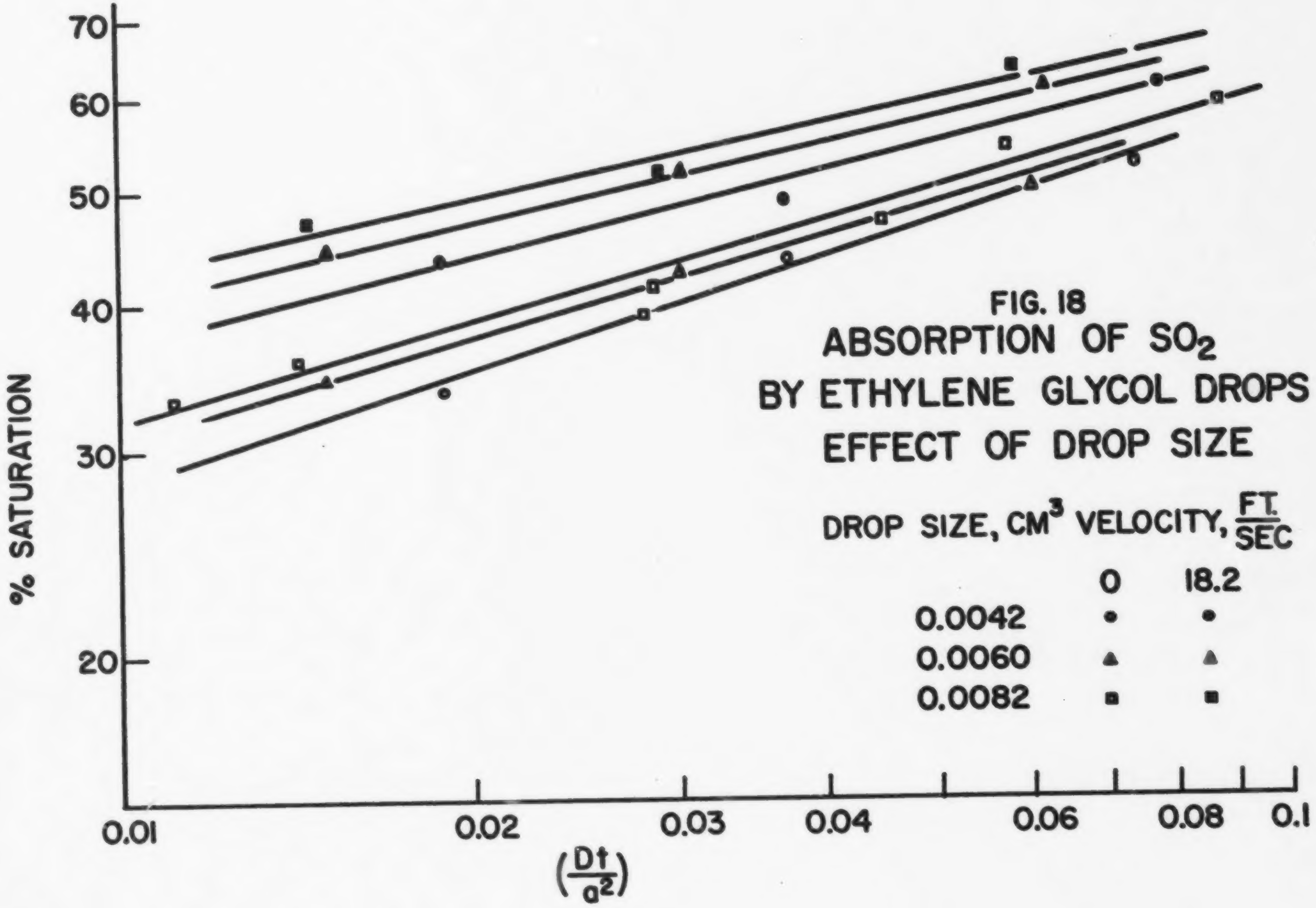


FIG. 18

ABSORPTION OF $SO_2$
BY ETHYLENE GLYCOL DROPS
EFFECT OF DROP SIZE

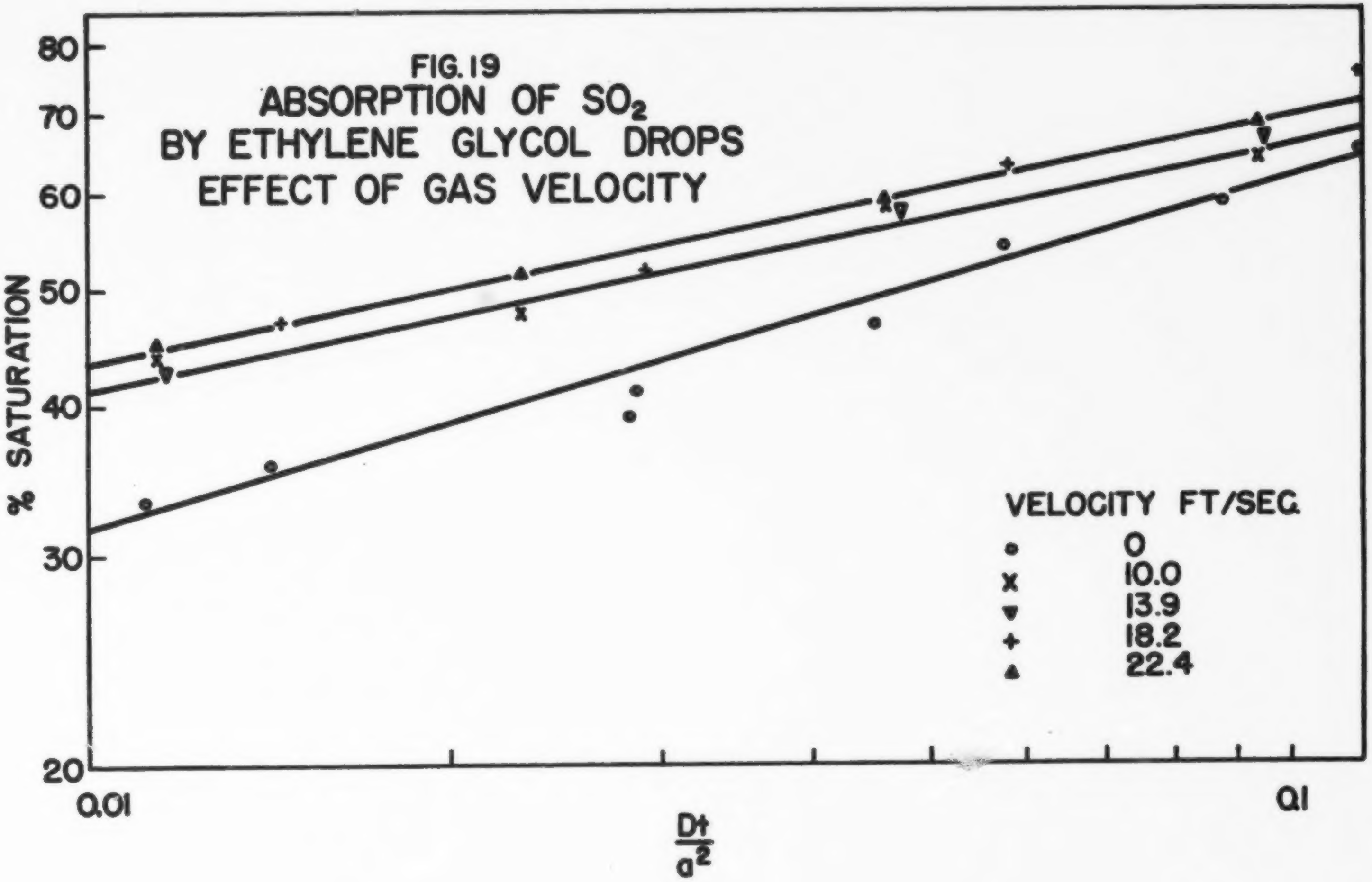


FIG. 19
ABSORPTION OF $SO_2$
BY ETHYLENE GLYCOL DROPS
EFFECT OF GAS VELOCITY

### 3. Circulation Velocities Inside Oscillating Drops

Circulation Velocities were determined by measuring the travel of aluminum particles near the surface of the drop and represent what is thought to be the maximum velocities. The measurements were made on projections of the motion pictures on a Vanguard Motion Analyzer.

The results are presented in Table 6 and are compared with the data of Garner and Lane[17]. The agreement with Garner's results is fair.

As can be seen from these data, the circulation velocity is essentially linearly related to the air velocity, as would be expected. The effect of viscosity on circulation velocity is very pronounced, as can be noted by comparing the different materials, and would be predicted by theory[21]. Finally, the larger drops show greater velocities of circulation for propylene glycol and ethylene glycol, again in accordance with theory[21]. The glycerine data do not show sufficient variation to warrant a similar conclusion in their particular case.

## C. FORCED CIRCULATION INSIDE OF A DROP

The preceding sections have shown the importance of internal circulation in drops on the mass transfer coefficient. It would be desirable to have a means of relating this increase in mass transfer rate to the internal circulation as would be a method of predicting the magnitude of such an effect.

A convenient way of expressing the increase of mass transfer rate is by means of an "effective diffusivity", which would be the

## TABLE 6

## INTERNAL CIRCULATION VELOCITIES

| Material | Drop Diameter | Air Velocity | Circulation Velocity |
|---|---|---|---|
| | cm. | ft./sec. | cm./sec. |
| 100% Propylene Glycol | 0.25 | 7.1 | 0.74 |
| | . . . | 12.3 | 0.79 |
| | . . . | 22.4 | 1.8 |
| | 0.25 | 7.1 | 1.5 |
| | . . . | 12.3 | 1.9 |
| | . . . | 22.4 | 2.8 |
| 80% Propylene Glycol | 0.287 | terminal | 1.9[17] |
| 100% Ethylene Glycol | 0.20 | 7.1 | 3.6 |
| | . . . | 12.3 | 4.4 |
| | . . . | 22.4 | 5.2 |
| | 0.25 | 7.1 | 4.8 |
| | . . . | 12.3 | 5.5 |
| | . . . | 22.4 | 6.4 |
| | 0.274 | terminal | 1.8[17] |
| 100% Glycerine | 0.20 | 6.3 | 0.11 |
| | . . . | 17.1 | 0.14 |
| | . . . | 22.4 | 0.19 |
| | . . . | 28.7 | 0.25 |
| | 0.225 | 12.3 | 0.13 |
| | . . . | 17.1 | 0.16 |
| | . . . | 22.4 | 0.19 |
| | 0.25 | 6.3 | 0.09 |
| | . . . | 12.3 | 0.14 |
| | . . . | 17.1 | 0.20 |
| | . . . | 22.4 | 0.18 |
| 80% Glycerol | 0.296 | terminal | 0.3[17] |

value the diffusivity constant would have to assume if the amount of material being transferred were transported by molecular diffusion.

The resistance to transfer inside of a sphere where bulk transport as well as molecular transport occurs may be considered as a "pseudo-film thickness", based on the Whitman "film model" concept[37]. Then, for any given change in the saturation of a sphere, we can compare the time that would be required for this change if it occurred through a small fixed laminar layer, to the time that would be required if it occurred in a stagnant sphere. It then follows, that we could also compare the effective diffusivity of this laminar film to the molecular diffusivity of the stagnant sphere if the same amount of material was transferred in both cases in the same time increment. This effective diffusivity of the film would depend upon its thickness which is related to the circulation velocity. If this pseudo-film thickness can be determined it would be possible to predict the effective diffusivity.

The following treatment develops the mathematical relationships necessary to apply this technique.

For mass transfer through a film,

$$N_A = D\frac{dc}{dx} \tag{7}$$

where $N_A$ = rate of transfer, mols/cm$^2$ sec; D = molecular diffusivity, cm$^2$/sec; c = concentration, mols/cm$^3$; x = film thickness, cm.

If we assume the holdup in film is negligible, and c = average concentration in sphere,

$$N_A = D\frac{(c_s - c)}{x} \tag{8}$$

where $c_s$ = surface concentration.

The change in concentration may be expressed as:

$$\frac{dc}{dt} = \frac{N_A A}{V_s} \tag{9}$$

where t = time, sec.; A = surface area, cm.$^2$; $V_s$ = volume of sphere, cm.$^3$. Substituting from above

$$\frac{dc}{dt} = \frac{D}{x}(c_s - c)\frac{(4\pi r^2)}{(4/3\pi r^3)} = \frac{3D}{rx}(c_s - c) \tag{10}$$

Rearranging

$$\frac{dc}{(c_s - c)} = \left(\frac{3D}{rx}\right) dt \tag{11}$$

Integrating

$$-\ln\left(\frac{c_s - c_2}{c_s - c_1}\right) = \left(\frac{3D}{rx}\right)(t_2 - t_1) \tag{12}$$

and

$$-\ln\left(\frac{c_s - c_2}{c_s}\right) = \left(\frac{3D}{rx}\right) t_2 \tag{13}$$

for $t_1 = 0$ and $c_1 = 0$

Now let F = fractional saturation = $\frac{c}{c_s}$ (14)

and

$$-\ln\left(\frac{c_s - c}{c_s}\right) = -\ln(1-F) = \left(\frac{3Dt}{rx}\right) \tag{15}$$

Thus, for any degree of saturation, F, we can calculate $\left(\frac{3Dt}{rx}\right)$. We also know for this saturation, F, $\left(\frac{Dt}{r^2}\right)$ for a stagnant sphere.

In going from any saturation $F_1$ to a saturation $F_2$ we have:

for the case of the laminar film

$$\left(\frac{3Dt}{rx}\right)_2 - \left(\frac{3Dt}{rx}\right)_1 = \Delta\left(\frac{3Dt}{rx}\right) \tag{16}$$

which we will call $\Delta\phi_1$.

for the case of a stagnant sphere

$$\left(\frac{Dt}{r^2}\right)_2 - \left(\frac{Dt}{r^2}\right)_1 = \Delta\left(\frac{Dt}{r^2}\right) \tag{17}$$

which we will call $\Delta\phi_2$.

From this we have a fixed mathematical relationship of $\Delta\phi_2/\Delta\phi_1$ for any particular increment of F under consideration. This is plotted in Figure 20.

In the case of a fixed laminar layer film

$$\Delta\phi_1 = \Delta\left(\frac{3Dt}{rx}\right) = \left(\frac{3D}{rx}\right)\Delta t \tag{18}$$

or,

$$\Delta t = \left(\frac{rx}{3D}\right)\Delta\phi_1 \tag{19}$$

For a stagnant sphere,

$$\Delta\phi_2 = \Delta\left(\frac{Dt}{r^2}\right) = \left(\frac{D_E}{r^2}\right)\Delta t \tag{20}$$

where $D_E$ = "effective" diffusivity for a similar time as for the film or

$$D_E = \left(\frac{r^2}{\Delta t}\right)\Delta\phi_2 \tag{21}$$

Substituting for $\Delta t$,

$$D_E = r^2\left(\frac{3D}{rx}\right)\frac{\Delta\phi_2}{\Delta\phi_1} = \left(\frac{3Dr}{x}\right)\frac{\Delta\phi_2}{\Delta\phi_1} \tag{22}$$

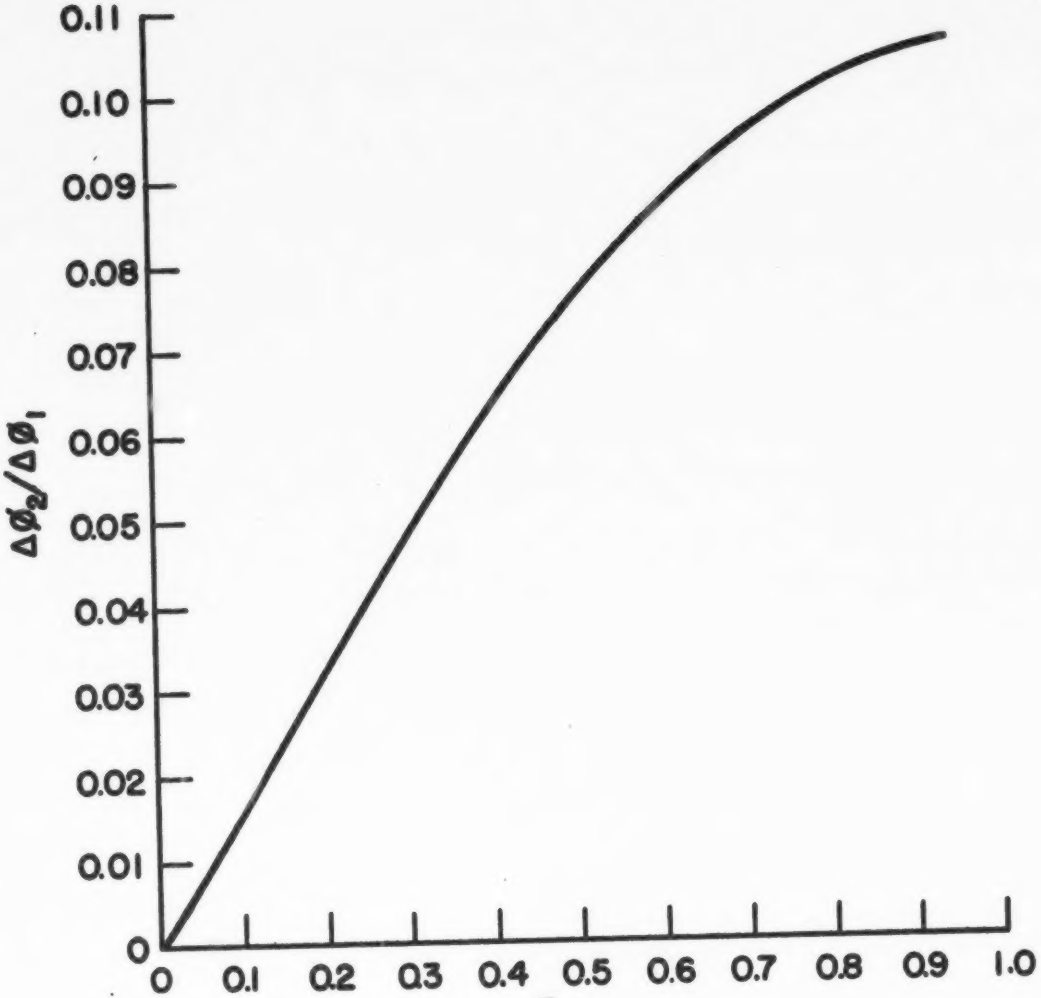


FIG. 20

$\Delta\emptyset_2/\Delta\emptyset_1$ vs. FRACTIONAL SATURATION

Then, the diffusivity ratio

$$R = \frac{D_E}{D} = \left(\frac{3r}{x}\right)\left(\frac{\Delta\phi_2}{\Delta\phi_1}\right) \tag{23}$$

The above relationship shows that the ratio R, for a given sphere and a given F value, is a function of the film thickness, which is controlled by the circulation velocity. This relationship is plotted in Figure 21.

By computing values of x from experimental data, we establish R. We can compute x from steady state measurement of absorption in liquid circulating through a sphere.

The rate of absorption of gas by such a sphere can be calculated as follows:

$$N_A = \frac{\Delta v_g}{A \Delta t} \tag{24}$$

where $\Delta v_g$ = volume of gas absorbed.

Since $x = \frac{D(c_s - c)}{N_A}$ from equation (8) (25)

substituting

$$x = AD(\Delta c)\frac{\Delta t}{\Delta v_g} = ADc_s \frac{(1-F_2)}{(\Delta v_g/\Delta t)} \tag{26}$$

since

$$\Delta c = (c_s - c_2) = c_s(1-F_2) \tag{27}$$

The value D can be obtained from literature, and the values of $\Delta c$ and $\left(\frac{\Delta v_g}{\Delta t}\right)$ can be experimentally measured for any velocity employed. Thus we can calculate x.

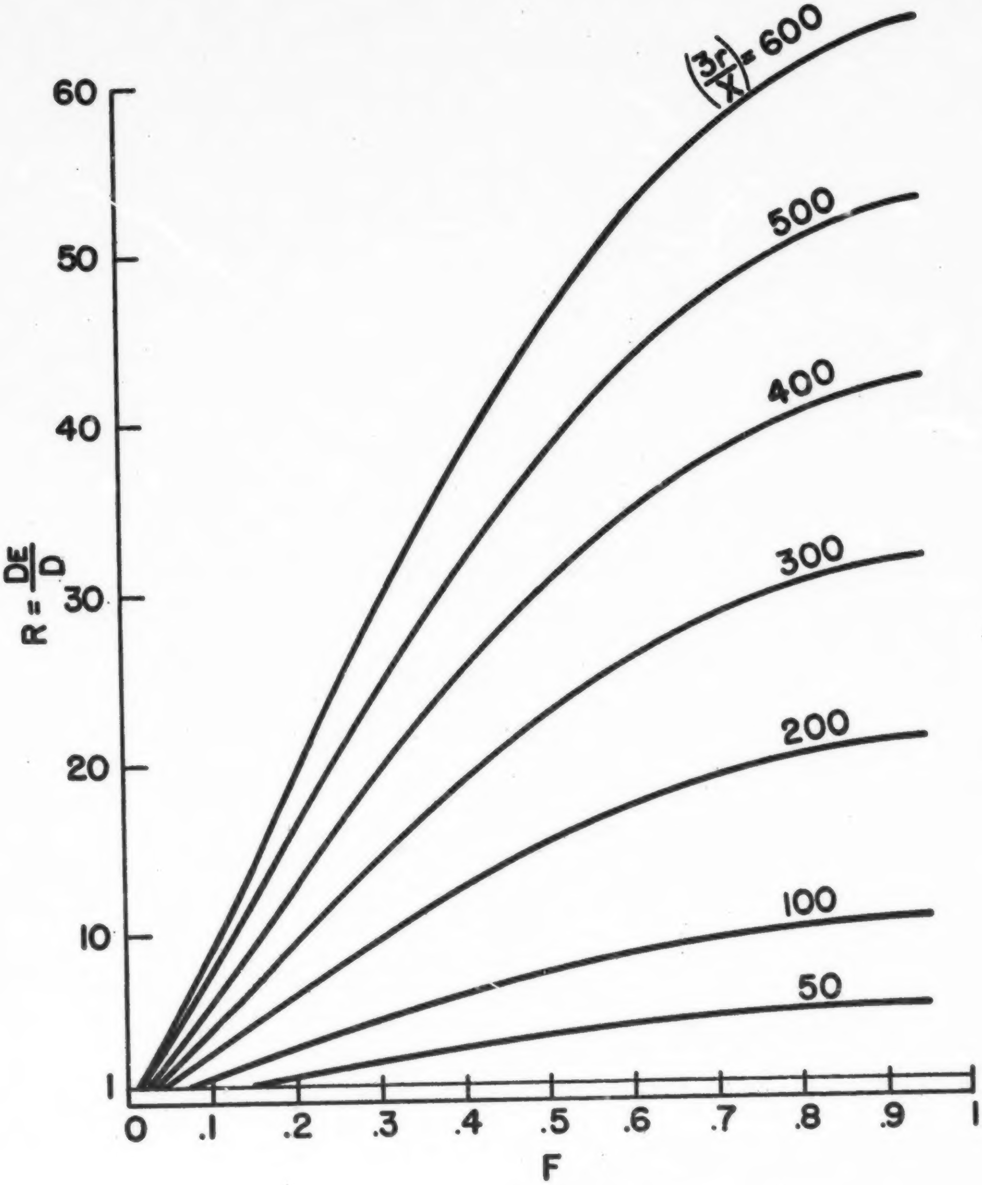


FIG. 21

DIFFUSIVITY RATIO R AS A
FUNCTION OF FRACTIONAL SATURATION

Since the values of x are related to the circulation velocity, the term $\frac{3r}{x}$ is also related to the circulation velocity in the same manner. Therefore, since R is related to $\frac{3r}{x}$, we have a means of relating R to circulation velocity.

The above treatment would say that for a specific drop size and a given circulation velocity we should be able to calculate a value of R.

The absorption data of $SO_2$ by $H_2O$ drops versus liquid velocity are plotted in Figure 22. By means of equation (26) the pseudo-film thickness was calculated and is plotted against liquid velocity in Figure 23. From these data, then, values of effective diffusivities can be calculated and used to predict absorption by oscillating drops.

Absorption data of $SO_2$ by propylene glycol drops are similarly treated and shown in Figures 25 and 24.

It is evident that the relationship of $\frac{3r}{x}$ versus velocity is not independent of other variables. An attempt to relate $\frac{3r}{x}$ to $N_{Re}$ was not successful, indicating that other factors (most likely surface tension) play important roles. The questionable nature of the calculated diffusivity for propylene glycol is recognized, but could not account for the entire difference. Additional work along this line will be necessary to establish a generalized correlation for $\frac{3r}{x}$.

The validity of any such relationship as the one here depends on how well it is supported by experimental evidence. This can be checked for the $SO_2$-propylene glycol system.

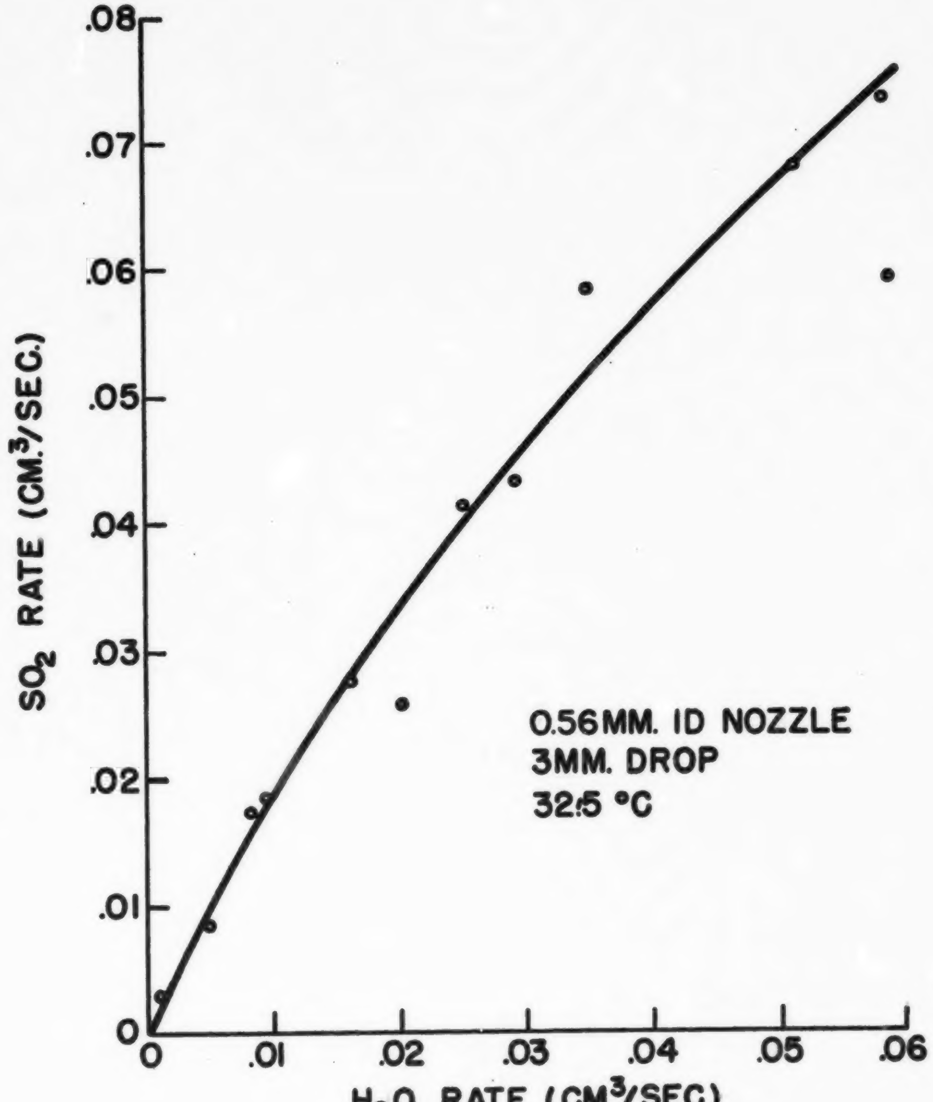


FIG. 22

$SO_2$ ABSORPTION RATE vs. $H_2O$ RATE

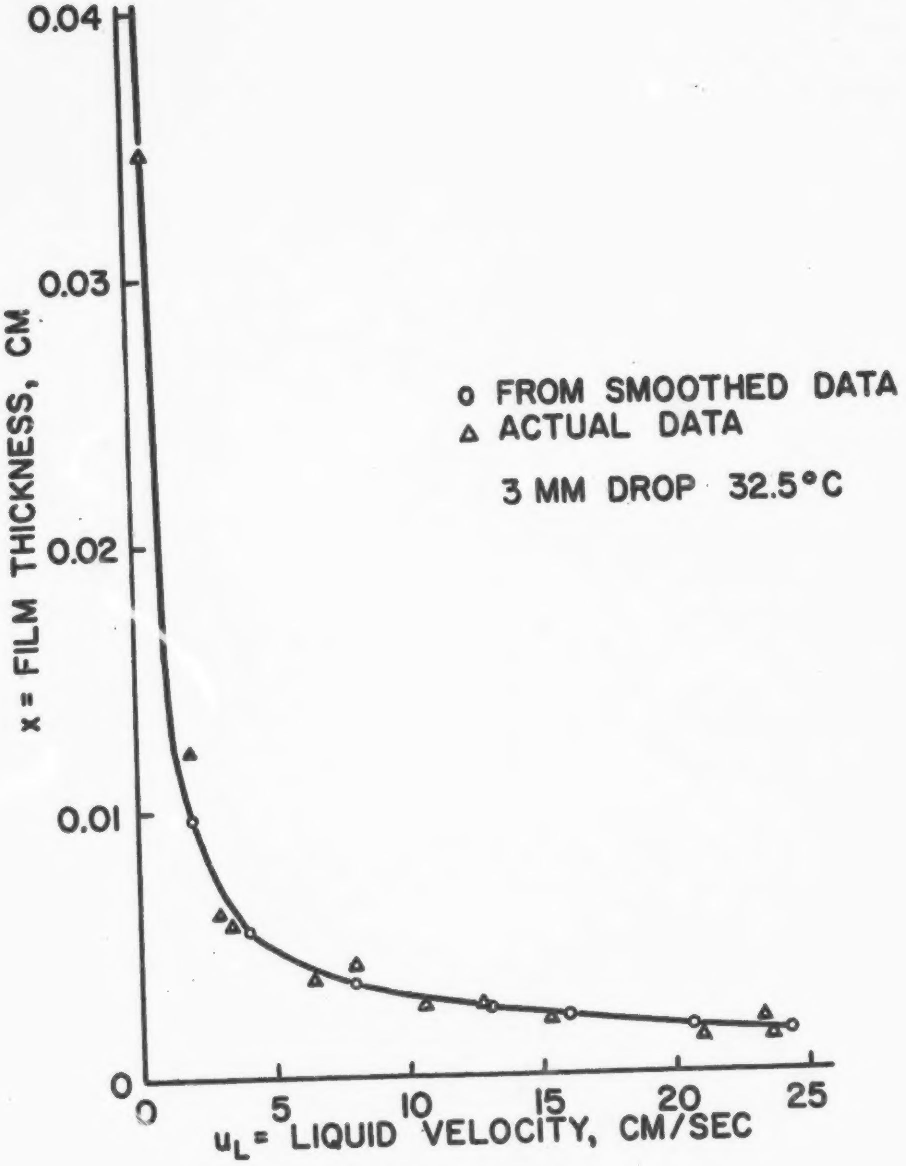


FIG. 23

PSEUDO FILM THICKNESS VERSUS LIQUID VELOCITY FOR $SO_2-H_2O$

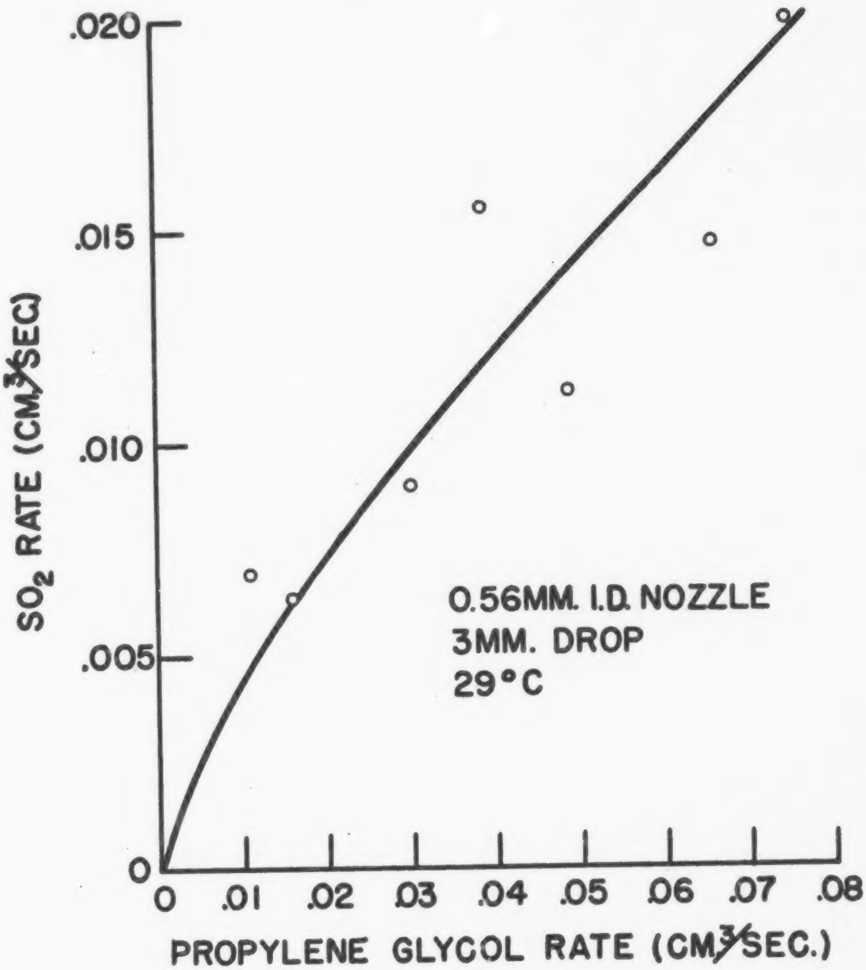


FIG. 24

$SO_2$ ABSORPTION RATE

VS.

PROPYLENE GLYCOL RATE

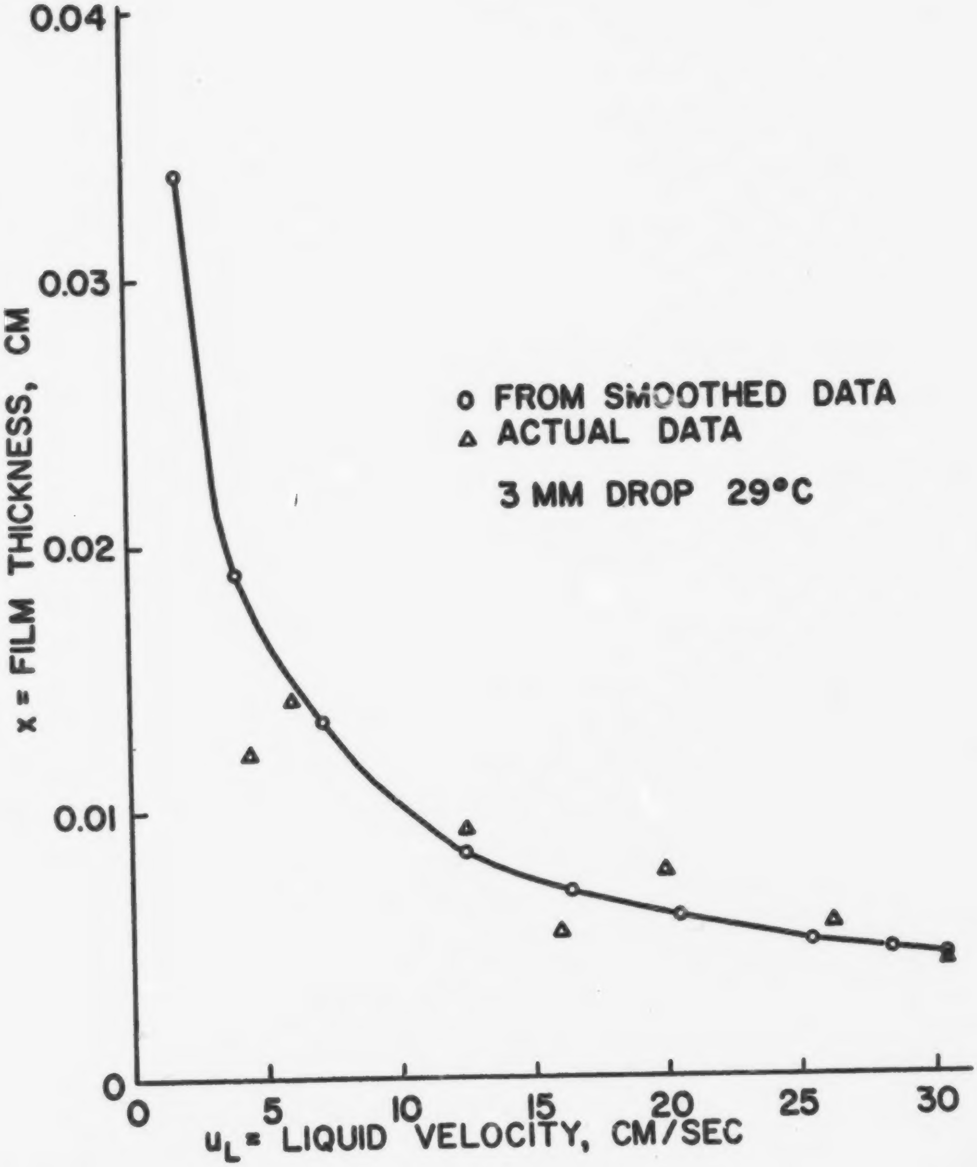


FIG. 25

PSEUDO FILM THICKNESS VERSUS LIQUID VELOCITY FOR $SO_2$ – PROPYLENE GLYCOL

Considering the more important region of high saturations, the oscillating drops exhibit an R of 1.9 when compared to stagnant drops at 75% saturation. For 0.25 cm. diameter drops at gas velocities of 22.4 ft./sec., the observed internal circulation velocity was 2.8 cm./sec. From Figures 25 and 21 we obtain a predicted value of 1.4. Although somewhat low, this value is of the correct order of magnitude. Considering the general nature of measurements in such an exploratory study as this, especially in the case of circulation velocity and the area of the forced circulation drop, it is significant that as good agreement as the above has been obtained.

The prediction technique does not hold as well for lower saturations. Whereas a lower R would be predicted at lower values of saturation, the contrary was obtained in this study. It is possible that at earlier stages other factors may play important roles. This was considered for the factor of increased surface in Section B. However, this effect becomes of small importance once the high saturations are reached, and is obscured.

## D. COMPARISON WITH OTHER STUDIES

The only published work reporting absorption of gases by drops that exhibit internal circulation is that of Garner and Lane[17]. Although other investigators[10, 20] have reported on the effect of turbulence on gas absorption by drops, their data could not be compared since they pertained to growing drops that were formed on the end of a capillary.

Garner and Lane report, among other materials, absorption of $CO_2$ by $H_2O$, and absorption of $H_2O$ by propylene glycol, and glycerol.

They have plotted their data for the $H_2O$-$CO_2$ system as the $\ln_e\left[(D_E-D) \times 10^5\right]$ versus the $\ln_e N_{Rei}$, getting a straight line relationship. The pseudo-film thickness relationship obtained in this work for $SO_2$-$H_2O$ is used to predict the effective diffusivity at a saturation of 50%, which is comparable to Garner's data on $CO_2$-$H_2O$ and is plotted on Figure 26. The data fall somewhat below the curve. The discrepancy cannot at this time be attributed to any recognized factor. However, since the relationship is an empirical one, and the systems being compared are different, it is quite possible that additional variables need be introduced into the correlation to make it more universal. Some support to this argument is obtained when one attempts to fit Garner's systems of $H_2O$-glycols to this curve and obtains significant deviations.

The propylene glycol-$SO_2$ data from this study have also been plotted on Figure 26, as have Garner's propylene glycol-$H_2O$ data. The degree of agreement between the two systems is of the same order but not as good as for the $CO_2$ systems. It should be noted that the propylene glycol data are for very low $N_{Re}$ values; it is quite possible that the model being considered is applicable only to the higher $N_{Re}$.

## E. CONCLUSIONS AND RECOMMENDATIONS

The objective of this study was to define the relationship of mass transfer to oscillation and internal circulation for the case of gas absorption by supported liquid drops. Three means by which oscillation would affect mass transfer were postulated as the outside coefficient, the areas, and the internal circulation of the drop.

It has been shown that oscillation does occur in supported drops and that it generally does increase the rate of mass transfer. Motion picture studies show that the oscillations are random and of two types, one of deformation and one of displacement, and that they increase with gas velocity. Measurements have been made, and thus provide at least an order of magnitude that can be expected, but are not precise enough to allow a generalized quantitative correlation of the effects of oscillation.

The effect of oscillation on the outside coefficient was found to be negligible under the conditions that represent oscillating drops. This extends to mass transfer the relation that has been observed in heat transfer; namely, that there is no effect when the vibrational velocity is less than the stream velocity.

Increases in area due to oscillation were expected to be small and to play a relatively minor role. Although it was found that these increases were small, indications are that they may play a fairly important part in the early stages of absorption, especially in systems such as the ones studied where internal circulation is not great. The exploratory nature of this study did not permit further definition of this factor.

Internal circulation was found to exist in oscillating drops, and velocities were measured. However, no quantitative relationship was obtained between the circulation velocity and the oscillations.

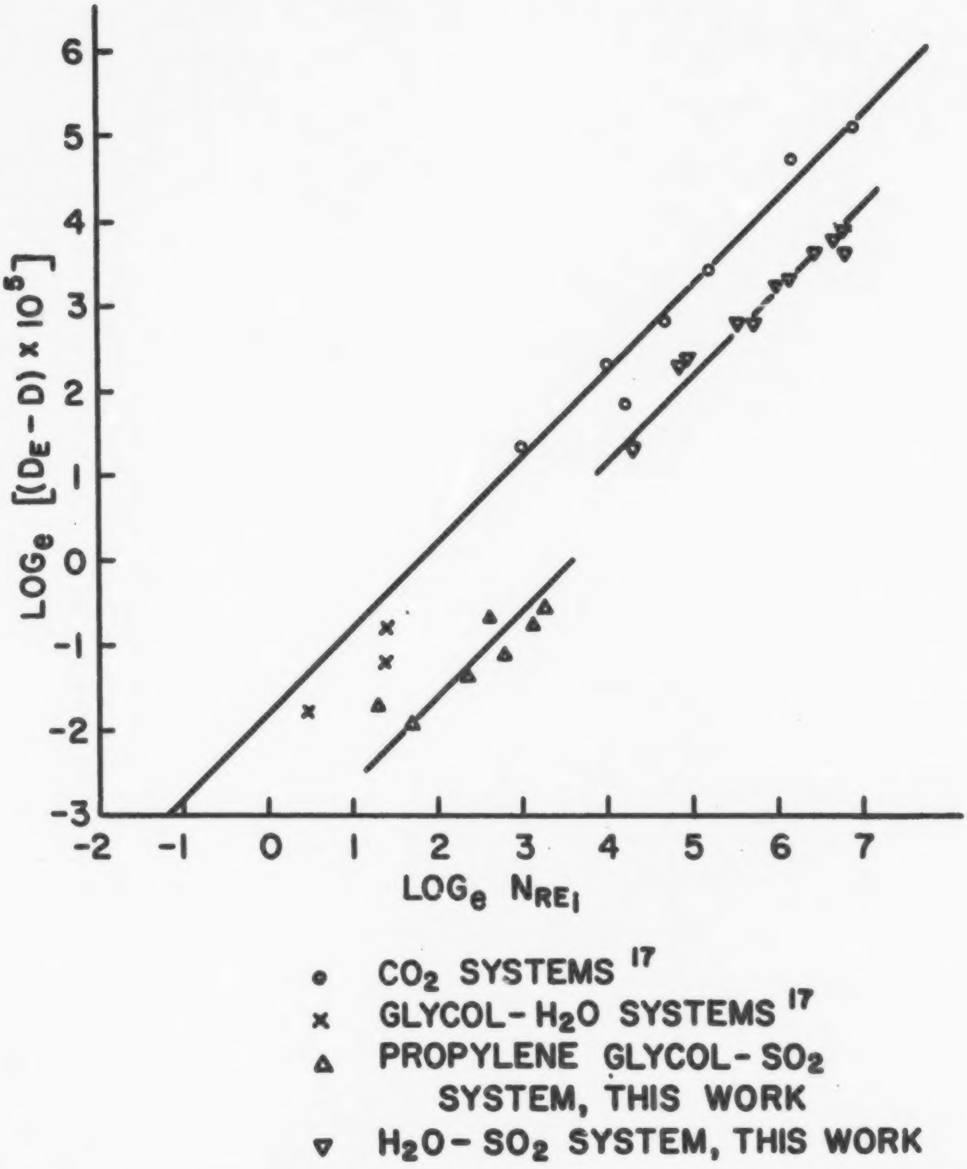


FIG. 26

EFFECT ON INTERNAL $N_{RE}$ ON EFFECTIVE DIFFUSIVITY

The variables that did seem to affect this velocity in a noticeable fashion were viscosity, drop size, and gas velocity, all in the manner expected. The effect of the internal circulation was to increase the rate of absorption. The particular systems examined exhibited relatively low circulation velocities, and the effects were nowheres near as great as would be expected in other liquids such as $H_2O$. The smallness of these effects prevented a more quantitative correlation.

Having established that oscillating drops exhibit internal circulation which increases rate of absorption, it was desired that there be a means of predicting the extent of increase caused by a given internal circulation. To this end, a technique was developed employing forced circulation through a suspended drop. By measuring the rate of absorption at a given liquid velocity, a pseudo-film thickness can be calculated for this velocity. The pseudo-film thickness can then be used to predict an effective diffusivity for the system under consideration. This technique was applied to two systems and the results compared with a relationship of effective diffusivity as a function of internal $N_{Re}$ that has been presented by Garner and Lane. The present status of the above technique necessitates data for each system under consideration. Additional work is required to arrive at a general correlation which will allow predictions from just the physical data of the materials.

From the above conclusions one would say that the objectives of this study have been attained to the following degree:

(1) Oscillation of supported drops has been shown to increase mass transfer by increased area and by internal circulation, but not by affecting the external coefficient. The results are semi-quantitative and do not permit a general correlation at this time.

(2) Frequencies and amplitudes of oscillation have been measured, but no quantitative relationship between them and mass transfer has been shown to exist.

(3) Internal circulation velocities have been measured and it is seen that the effective diffusivity depends on internal circulation velocity.

(4) A new technique has been developed that allows prediction of an effective diffusivity for a given circulation velocity in a specific material.

It is felt that the above results represent a reasonable attainment of the objectives. The exploratory nature of the present study suggests certain areas of work that would be desirable in extending the above results. These might include the following:

(1) A more extensive study of the area effects during the initial period of absorption.

(2) A more extensive study of the relationship of the physical properties of the system to oscillation and internal circulation, leading to a generalized correlation. A

study of $H_2O$ drops would be especially desirable.

(3) More precise measurements to allow a quantitative relationship between oscillation and effective diffusivity.

(4) Extension of the forced-circulation-through-a-drop studies to establish the effect of such variables as drop size, degree of saturation, and physical properties, leading to a generalized correlation for predicting effective diffusivity.

# SUMMARY

The present study on gas absorption by oscillating drops has shown that oscillation can increase the rate of mass transfer by means of deformation and internal circulation in the cases where liquid phase resistance controls. The increase, expressed as an "effective diffusivity", depends on circulation velocity within the drop, and can be negligible or small in the cases of viscous materials such as those studied here. Materials such as $H_2O$ would exhibit much greater effects.

No effect of oscillation is noted on the outside resistance when the vibration velocity is less than the gas velocity; this is in agreement with studies on heat transfer. Since the maximum vibrational velocities that can exist in real systems undergoing oscillation are much lower than the gas velocities needed to cause oscillation, it is reasonable to expect that no likelihood exists for an increase of gas film coefficient due to drop oscillation.

The technique of forced circulation through a drop presents a new means of measuring the effect of liquid velocity inside of a drop. By such measurements it is possible to predict effective diffusivities for any material that exhibits circulation in its drop form.

The present state of this technique employs calculation of a pseudo-film thickness which is dependent on the circulation velocity, having a different dependency for each material. It is hoped that additional studies will establish the other important variables so that a generalized correlation may result which will allow prediction of effective diffusivity without the necessity of measurements.

# NOMENCLATURE

a = radial distance from center of sphere, cm.
A = area, cm.$^2$
c = concentration, gm. mols. $SO_2$/liter solution
$c'$ = concentration, gm. mols. $SO_2$/gm. solvent
$c_{sat}$ = saturated concentration
d = diameter, cm.
$D_E$ = effective diffusivity, cm.$^2$/sec.
$D_L$ = molecular diffusivity in liquid, cm.$^2$/sec.
$D_V$ = molecular diffusivity in vapor, ft.$^2$/hr.
e = exponential
f = frequency
F = fractional degree of saturation
k = constant
$k_c$ = transfer coefficient, ft/hr.
$k_g$ = gas phase mass transfer coefficient, mols./hr. ft.$^2$ atm.
m = mass, gm.
M = molecular weight of solvent
n = mols.
$N_A$ = rate of transfer of component A, mols./cm.$^2$ sec.
$N_{Re}$ = Reynolds Number = $(Du\rho/\mu)$
$N_{Sc}$ = Schmidt No. = $(\mu/\rho D_v)$
p = pressure, atm.
r = radius of drop, cm.
R = ratio of effective to molecular diffusivity $(D_E/D)$
t = time, sec.
T = absolute temperature, °K
$u_L$ = (liquid) circulation velocity, cm./sec.
$u_V$ = vibrational velocity, ft./sec.
$v_G$ = volume of gas, cm.$^3$
$v_L$ = volumetric liquid flow rate, cm.$^3$/sec.
$V_1$ = molal volume of a solute at its normal boiling point, cm.$^3$/mol
x = film thickness, cm.
W = lbs.
X, Y, Z = rectangular coordinates, amplitudes, cm.

## Greek Letters

$\Delta\phi_1 = \Delta\left(\frac{3Dt}{rx}\right)$
$\Delta\phi_2 = \Delta\left(\frac{Dt}{r^2}\right)$
$\epsilon$ = force constant
$\mu$ = absolute viscosity, centipoises
$\nu$ = kinemetric viscosity, csks.
$\rho$ = density, gm./cm.$^3$
$\sigma$ = surface tension, dynes/cm.$^2$
$\chi$ = association parameter
$\Omega_D$ = collision integral

## Subscripts

1 = initial
2 = final
g = gas
l = liquid
i = inside
o = outside
s = surface

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## APPENDIX I

## SUBLIMATION OF NAPHTHALENE SPHERES

Vapor pressure of naphthalene solid (I.C.T., III, p.208) 0-80°C.

$$\log_{10} P_{mm} = -\frac{3729.3}{T°K} + 11.450$$

at $50°C = 323.15°K$

$$\log_{10} P_{mm} = -\frac{3729.3}{323.15} + 11.450$$

$$= -11.540 + 11.450 = -0.090$$

$$p = 0.813 \text{ mm. Hg} = 0.00107 \text{ atm.}$$

Diffusivity of naphthalene-air gas system:

$$D = 0.0611 \frac{cm^2}{sec.} \text{ at } 25°C., 1 \text{ atm.}$$

(Robert C. Reid and Thomas K. Sherwood, "The Properties of Gases and Liquids", McGraw-Hill Book Co. Inc., New York, 1959 p. 274)

To estimate it at another temperature use the following relationship:

$$D_v \text{ at } T_2 = (D_v \text{ at } T_1)\left(\frac{T_2}{T_1}\right)^{3/2} \frac{\Omega_D \text{ at } T_1}{\Omega_D \text{ at } T_2} \qquad \text{(ibid., p. 280)}$$

at 25°C. $T_1 = 298°K$

at 50°C. $T_2 = 323°K$

$\Omega_D$ is a function of $\frac{kT}{\epsilon}$ (ibid. p. 269)

for air, $\frac{\epsilon}{k} = 97$ (ibid. p. 270)

| $T \times \frac{k}{\epsilon}$ | D |
|---|---|
| 298 X 1/97 = 3.07 | 0.9431 |
| 323 X 1/97 = 3.33 | 0.9233 |

$$D_v \text{ at } 50^\circ\text{C.} = (0.0611)\frac{\text{cm.}^2}{\text{sec.}}\left(\frac{323}{298}\right)^{3/2}\left(\frac{0.9431}{0.9233}\right) \times \frac{(3600)}{(30.5)^2}\,\frac{\frac{\text{sec.}}{\text{hr.}}}{\frac{\text{cm.}^2}{\text{ft.}^2}} =$$

$$0.273\ \frac{\text{ft.}^2}{\text{hr.}}$$

For calculation of mass transfer coefficients in forced convection gas phase, use Frossling's correlation:

$$\frac{k_c d}{D_v} = 2.0\left[1 + 0.276 N_{R_e}^{1/2} N_{S_c}^{1/3}\right] \quad \text{where } k_g = \frac{k_c}{RT}$$

$$\therefore\ k_g = \frac{(2.0)D_v}{dRT}\left[1 + 0.276 N_{R_e}^{1/2} N_{S_c}^{1/3}\right] \frac{\text{mols}}{\text{hr. ft.}^2\text{ atm.}}$$

$$= 2.74\frac{D_v}{dT}\left[1 + 0.276 N_{R_e}^{1/2} N_{S_c}^{1/3}\right] \frac{\text{mols}}{\text{hr. ft.}^2\text{ atm.}}$$

where $T = {}^\circ R$

Since the gas is essentially pure air, use the physical properties of air.

at 50°C.

$$\text{density } \rho = 0.0682\ \frac{\text{lbs.}}{\text{ft.}^3}$$

$$\text{viscosity } \mu = 0.0190 \text{ centipoises}$$

$$= 0.0460\ \frac{\text{lbs. ft.}}{\text{hr.}}$$

[Perry, J. (ed.), "Chem. Eng. Hdbk.", 3rd ed., McGraw-Hill Book Co. Inc. New York, p. 371)

$$N_{S_c} = \frac{\mu}{\rho D_v} = \frac{(0.0460)\ \frac{\text{lbs. ft.}}{\text{hr.}}}{(0.0682)\ \frac{\text{lbs.}}{\text{ft.}^3}\ (0.273)\ \frac{\text{ft.}^2}{\text{hr.}}} = 2.47$$

$$N_{S_c}^{1/3} = (2.47)^{1/3} = 1.35$$

$$\therefore k_g = \frac{(2.74)(0.273)}{d(582)}\left[1 + 0.276 N_{R_e}^{1/2}(1.35)\right] =$$

$$\frac{1.39 \times 10^{-3}}{d}\left[1 + 0.373 N_{R_e}^{1/2}\right]\frac{\text{mols}}{\text{hr. ft.}^2\ \text{atm.}}$$

where d = ft., diameter of sphere

For calculation of experimental values of $k_g$ at 50°C.

let $N_A = k_g(p_i - p_g) = \frac{\text{lbs. mols}}{\text{hr. ft.}^2}$

also $\frac{dn}{dt} = N_A A = k_g A(p_i - p_g)\ \frac{\text{lbs. mols}}{\text{hr.}}$

$= k_g A p_i$ since gas stream concentration of naphthalene is essentially zero.

for short periods, $\frac{dn}{dt} \simeq \frac{\Delta n}{\Delta t}$

$$\therefore k_g = \left(\frac{\Delta n}{\Delta t}\right)\left(\frac{1}{Ap_i}\right)\frac{\text{lbs. mols}}{\text{hr. ft.}^2\ \text{atm.}}$$

Assume that samples are essentially spheres $\therefore A = \pi d^2$

$$k_g = \left(\frac{\Delta n}{\Delta t}\right)\left(\frac{1}{\pi d^2 p_i}\right)$$

$$= \left(\frac{\Delta w}{\Delta t}\right)\frac{\text{gm.}}{\text{min.}}\left(\frac{1}{128.16}\right)\frac{\text{gm. mol.}}{\text{gm.}}\left(\frac{1}{454}\right)\frac{\text{lbs.}}{\text{lb. mol}}\left(\frac{1}{\pi d^2}\right)\frac{1}{\text{cm.}^2}$$

$$(30.5)^2\frac{\text{cm.}^2}{\text{ft.}^2}\left(\frac{1}{0.00107}\right)\frac{1}{\text{atm.}}\left(\frac{60}{1}\right)\frac{\text{min.}}{\text{hr.}}$$

$$k_g = \frac{2.85 \times 10^3}{d^2}\left(\frac{\Delta w}{\Delta t}\right)$$

where d = cm.

$\Delta w$ = gm.

t = min.

## TABLE 7

## SUBLIMATION OF NAPHTHALENE SPHERES

| Sphere | Velocity | Frequency | $\Delta w$ | $\Delta t$ | $\frac{\Delta w}{\Delta t}$ | $k_g$ |
|---|---|---|---|---|---|---|
| mm. | $\frac{ft.}{sec.}$ | c.p.s. | gm. | min. | $\frac{gm.}{min.}$ | $\frac{lb.\ mol}{hr.ft^2.atm.}$ |
| 6.80 | 25 | 0 | 0.0042 | 2 | 0.00210 | 1.29 |
| 6.75 | 25 | 0 | .0064 | 3 | .00213 | 1.33 |
| 6.65 | 25 | 0 | .0080 | 4 | .00200 | 1.29 |
| 6.55 | 25 | 10 | .0039 | 2 | .00195 | 1.30 |
| 6.50 | 25 | 10 | .0056 | 3 | .00187 | 1.26 |
| 6.45 | 25 | 10 | .0037 | 2 | .00185 | 1.27 |
| 5.90 | 25 | 0 | .0047 | 3 | .00157 | 1.28 |
| 5.80 | 25 | 0 | .0062 | 4 | .00155 | 1.31 |
| 8.00 | 25 | 0 | .0050 | 2 | .00250 | 1.11 |
| 7.90 | 25 | 0 | .0080 | 3 | .00267 | 1.22 |
| 9.70 | 15 | 0 | .0079 | 3 | .00263 | 0.80 |
| 9.65 | 15 | 0 | .0071 | 3 | .00237 | 0.73 |
| 9.60 | 15 | 18 1/3 | .0071 | 3 | .00237 | 0.73 |
| 9.55 | 15 | 18 1/3 | .0068 | 3 | .00227 | 0.71 |
| 9.50 | 15 | 0 | .0068 | 3 | .00227 | 0.72 |
| 9.45 | 5 | 0 | .0071 | 5 | .00142 | 0.45 |
| 9.40 | 5 | 0 | .0060 | 4 | .00150 | 0.48 |
| 9.35 | 5 | 13 2/3 | .0054 | 4 | .00135 | 0.44 |
| 8.05 | 5 | 0 | .0056 | 5 | .00112 | 0.49 |
| 8.00 | 5 | 0 | .0059 | 5 | .00118 | 0.53 |
| 7.95 | 5 | 15 | .0063 | 5 | .00126 | 0.57 |
| 7.90 | 5 | 15 | .0059 | 5 | .00118 | 0.54 |
| 6.00 | 5 | 0 | .0041 | 5 | .00082 | 0.65 |
| 5.95 | 5 | 0 | .0035 | 4 | .00087 | 0.70 |
| 5.90 | 5 | 16 | .0043 | 5 | .00086 | 0.71 |
| 5.85 | 5 | 20 | .0044 | 5 | .00088 | 0.73 |
| 5.80 | 15 | 0 | .0063 | 5 | .00126 | 1.07 |
| 5.75 | 15 | 16 | .0063 | 5 | .00126 | 1.08 |
| 7.75 | 15 | 0 | .0108 | 5 1/2 | .00197 | 0.93 |
| 7.65 | 15 | 0 | .0112 | 5 1/2 | .00203 | 0.99 |
| 7.60 | 15 | 15 | .0112 | 5 1/2 | .00203 | 1.00 |
| 10.40 | 15 | 0 | .0122 | 4 | .00305 | 0.80 |
| 10.30 | 15 | 0 | .0089 | 3 | .00297 | 0.80 |
| 10.20 | 15 | 16 | .0083 | 3 | .00277 | 0.76 |
| 10.10 | 15 | 16 | 0.0086 | 3 | 0.00287 | 0.80 |

# APPENDIX II

## PHYSICAL PROPERTIES

### TABLE 8

### SOLUBILITY OF $SO_2$

| Ref. | Temp. | Time | $c_{sat.}$ | $c'_{sat.}$ |
|---|---|---|---|---|
| | °C | Hrs. | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{\text{mols } SO_2}{\text{1000 gm. Glycerine}}$ |
| | | | In Glycerine | |
| I-108 | 31.3 | 8 | 1.03 | 0.86 |
| I-111 | 24.0 | 12 | 1.24 | 1.05 |
| I-119 | 29.5 | 28 | 0.98 | 0.81 |
| I-125 | 25.0 | 18 | 1.19 | 1.00 |
| II-30 | 30.0 | 60 | 1.07 | 0.90 |
| II-58 | 40.0 | 29 | 0.81 | 0.68 |
| | | | In Propylene Glycol | |
| II-38 | 25.0 | 15 | 1.89 | 1.95 |
| II-42 | 30.0 | 44 | 1.54 | 1.57 |
| II-44 | 25.0 | 41 | 1.94 | 2.00 |
| II-50-1 | 40.0 | 12 | 1.02 | 1.03 |
| II-50-7 | 40.0 | 17 | 0.99 | 1.00 |
| II-51 | 30.0 | 17 | 1.48 | 1.51 |

TABLE 8--Continued

| Ref. | Temp. | Time | $c_{sat.}$ | $c'_{sat.}$ |
|---|---|---|---|---|
| | °C | Hrs. | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{\text{mols } SO_2}{\text{1000 gm. Glycerine}}$ |
| In Ethylene Glycol | | | | |
| II-4 | 25.0 | 54 | 2.75 | 2.77 |
| II-17 | 30.0 | 13 | 2.30 | 2.28 |
| II-23 | 30.0 | 20 | 2.25 | 2.23 |
| II-25 | 30.0 | 39 | 2.20 | 2.18 |
| II-35 | 24.0 | 13 | 2.66 | 2.68 |
| II-53-78 | 40.0 | 15 | 1.62 | 1.57 |

## TABLE 9

## VISCOSITY OF GLYCERINE-$SO_2$ SOLUTIONS

## VISCOMETER TUBE - 500 SERIES - F549

## TUBE CONSTANT = 5.56 CSKS/SEC.

| Ref. | Temp. | Conc. | Efflux | Visc. | Density | Visc. |
|---|---|---|---|---|---|---|
| | °C | $\frac{\text{mols } SO_2}{\text{ml soln.}}$ | Time | csks. | $\frac{\text{gm.}}{\text{cm.}^3}$ | cps. |
| | | $X\ 10^3$ | Sec. | $\nu = kt$ | | $\eta = \nu d$ |
| II-14 | 25 | 1.20 | 32.2 | 179 | 1.2693 | 227 |
| | 25 | 0.61 | 45.2 | 251 | 1.2595 | 316 |
| | 25 | 0.30 | 53.1 | 295 | 1.2543 | 370 |
| | 25 | 0 | 63.7 | 354 | 1.2493 | 442 |
| II-30 | 30 | 1.02 | 21.5 | 120 | 1.2633 | 152 |
| | 30 | 0.52 | 30.1 | 167 | 1.2549 | 209 |
| | 30 | 0.26 | 34.6 | 193 | 1.2505 | 241 |
| | 30 | 0 | 41.0 | 228 | 1.2481 | 285 |
| II-59 | 40 | 0.81 | 9.1 | 51 | 1.2533 | 64 |
| | 40 | 0.40 | 14.0 | 77.8 | 1.2471 | 97 |
| | 40 | 0.20 | 17.4 | 96.8 | 1.2440 | 120 |
| | 40 | 0 | 21.7 | 121 | 1.2410 | 150 |

## TABLE 10

## VISCOSITY OF PROPYLENE GLYCOL-$SO_2$ SOLUTIONS

VISCOMETER TUBE 300 SERIES - D317

TUBE CONSTANT = 0.309 CSKS/SEC.

| Ref. | Temp. | Conc. | Efflux | Visc. | Density | Visc. |
|---|---|---|---|---|---|---|
| | °C | $\frac{\text{mols } SO_2}{\text{ml soln.}}$ | Time | csks | $\frac{\text{gm.}}{\text{cm.}^3}$ | cps. |
| | | X $10^3$ | sec. | $\nu=kt$ | | $\eta=\nu d$ |
| II-38 | 25 | 1.90 | 45.2 | 14.0 | 1.0915 | 15.3 |
| | 25 | 1.00 | 81.2 | 25.1 | 1.0640 | 26.7 |
| | 25 | 0.50 | 110.2 | 34.1 | 1.0490 | 35.8 |
| II-36 | 25 | 0 | 142.1 | 43.8 | 1.0337 | 45.3 |
| II-44 | 25 | 1.90 | 46.1 | 14.3 | 1.0915 | 15.6 |
| | 25 | 0.97 | 83.6 | 25.8 | 1.0628 | 27.4 |
| | 25 | 0.43 | 116.6 | 36.0 | 1.0468 | 37.7 |
| II-42 | 30 | 1.50 | 41.3 | 12.8 | 1.0752 | 13.8 |
| | 30 | 0.73 | 66.3 | 20.5 | 1.0518 | 21.5 |
| | 30 | 0.37 | 89.5 | 27.6 | 1.0413 | 28.7 |
| | 30 | 0 | 111.2 | 34.4 | 1.0303 | 35.5 |
| II-50 | 40 | 1.00 | 29.2 | 9.03 | 1.0521 | 9.50 |
| | 40 | 0.50 | 44.3 | 13.7 | 1.0377 | 14.2 |
| | 40 | 0.25 | 52.4 | 16.2 | 1.0306 | 16.7 |
| II-49 | 40 | 0 | 69.5 | 21.5 | 1.0236 | 22.0 |

## TABLE 11

## VISCOSITY OF ETHYLENE GLYCOL-$SO_2$ SOLUTIONS

## VISCOMETER TUBE 300 SERIES - D317

## TUBE CONSTANTS 0.309 CSKS./SEC.

| Ref. | Temp. | Conc. | Efflux | Visc. | Density | Visc. |
|---|---|---|---|---|---|---|
| | °C | mols $SO_2$ / ml. soln. | Time | Csks. | $\frac{gm.}{cm.^3}$ | cps. |
| | | X $10^3$ | sec. | $\nu=kt$ | | $\eta=\mu d$ |
| II-13 | 25 | 2.65 | 25.3 | 7.82 | 1.1646 | 9.10 |
| | 25 | 1.34 | 35.9 | 11.0 | 1.1365 | 12.5 |
| | 25 | 0.67 | 43.0 | 13.3 | 1.1230 | 14.9 |
| | 25 | 0 | 50.8 | 15.7 | 1.1090 | 17.4 |
| II-26 | 30 | 2.25 | 23.3 | 7.20 | 1.1525 | 8.31 |
| | 30 | 1.18 | 31.5 | 9.73 | 1.1300 | 11.0 |
| | 30 | 0.59 | 35.0 | 10.8 | 1.1180 | 12.1 |
| | 30 | 0 | 41.3 | 12.8 | 1.1056 | 14.2 |
| II-53 | 40 | 1.60 | 18.1 | 5.60 | 1.1350 | 6.36 |
| | 40 | 0.80 | 23.2 | 7.16 | 1.1175 | 8.01 |
| | 40 | 0.41 | 26.0 | 8.05 | 1.1085 | 8.92 |
| | 40 | 0 | 28.7 | 8.85 | 1.0998 | 9.73 |

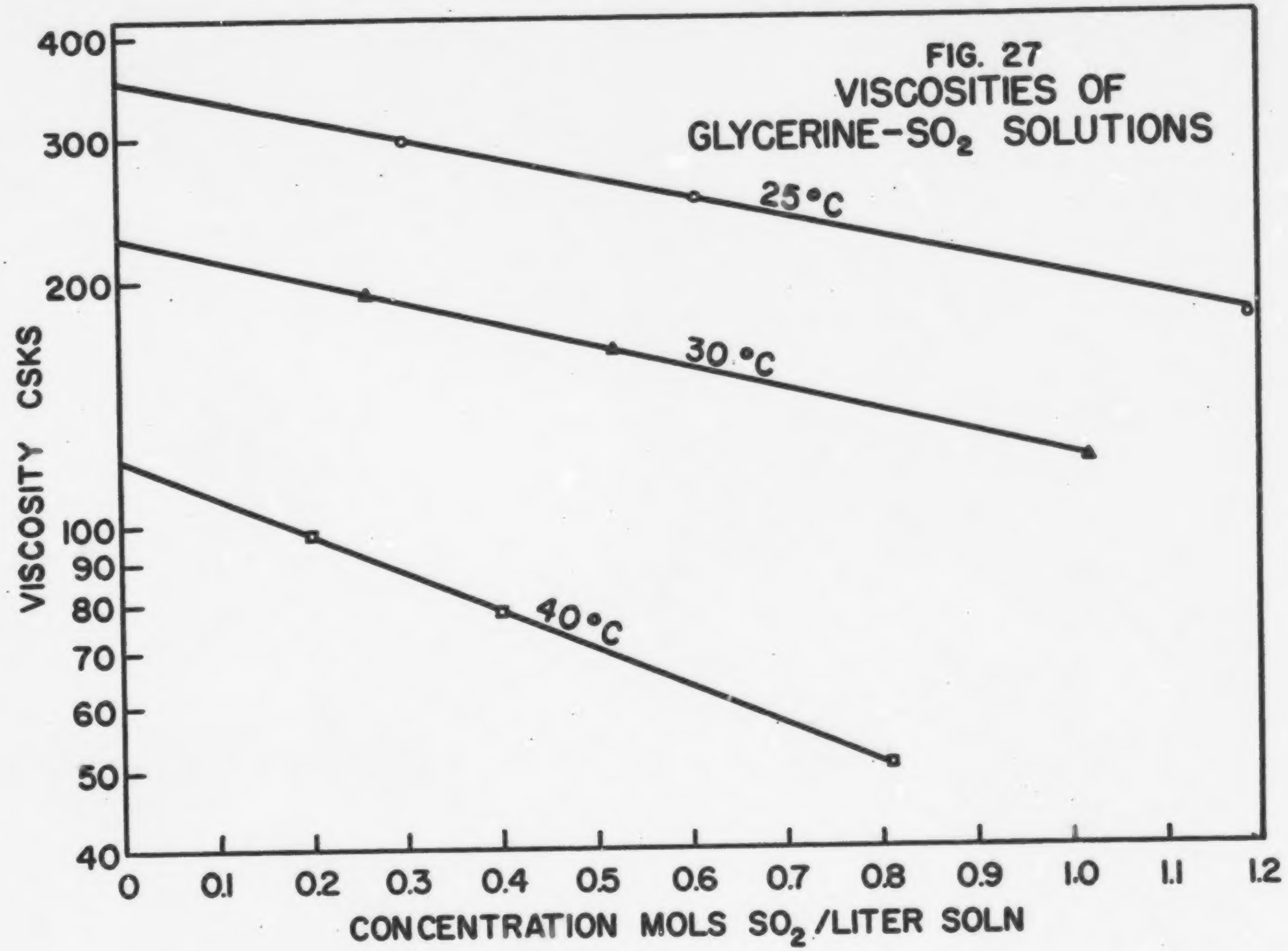

FIG. 27
VISCOSITIES OF
GLYCERINE-$SO_2$ SOLUTIONS

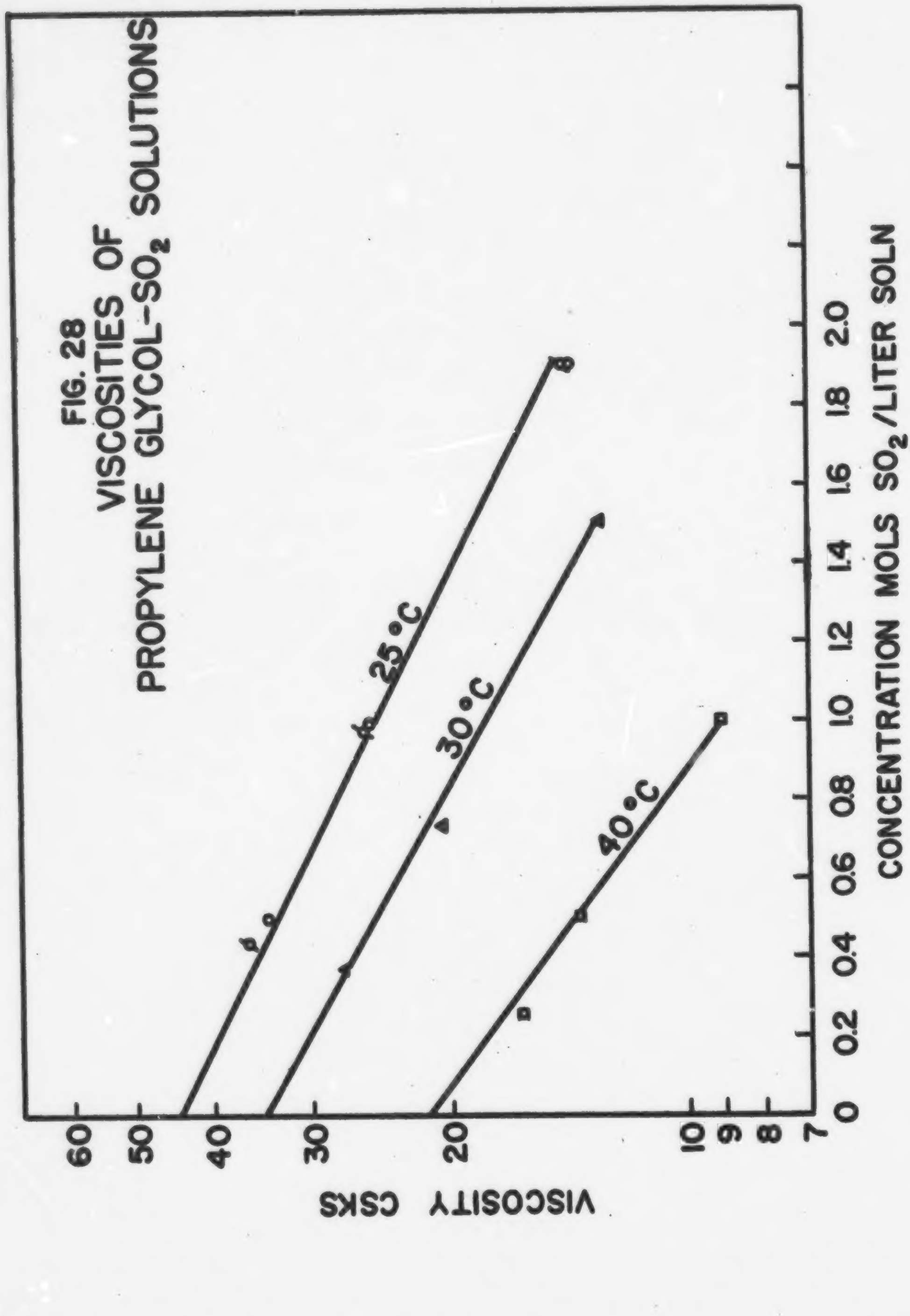

FIG. 28
VISCOSITIES OF
PROPYLENE GLYCOL-$SO_2$ SOLUTIONS

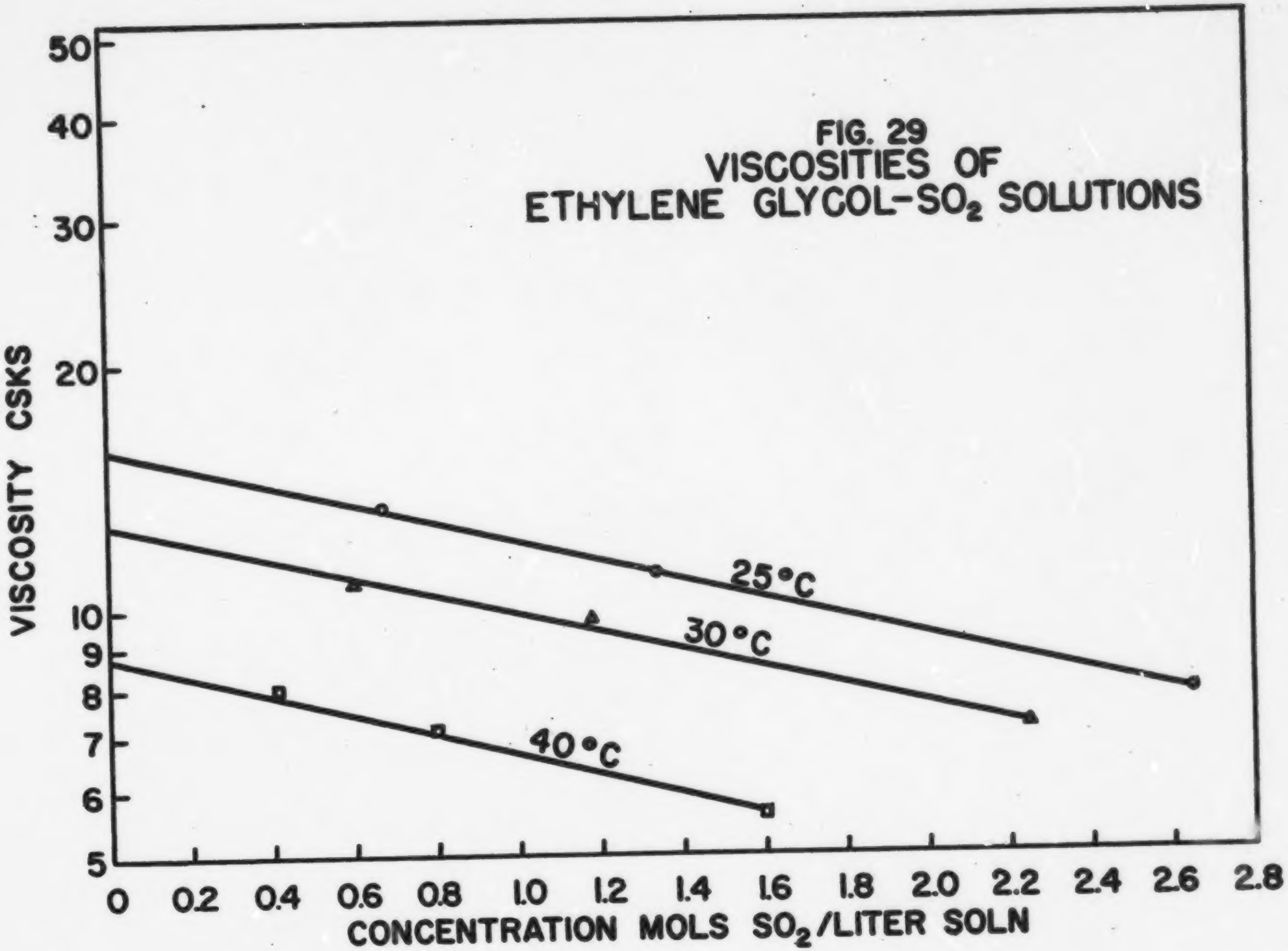

FIG. 29
VISCOSITIES OF
ETHYLENE GLYCOL-$SO_2$ SOLUTIONS

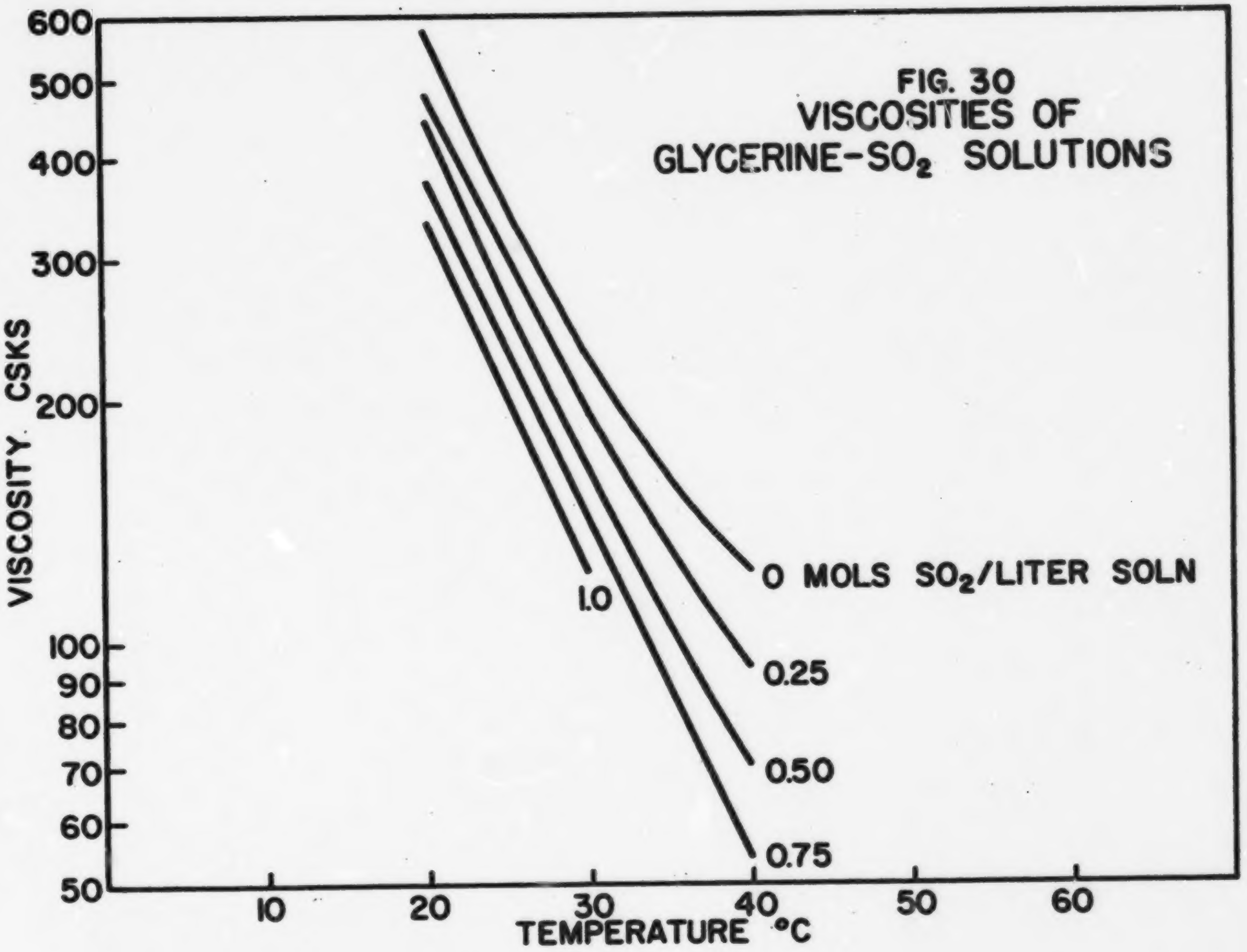

FIG. 30
VISCOSITIES OF
GLYCERINE-$SO_2$ SOLUTIONS

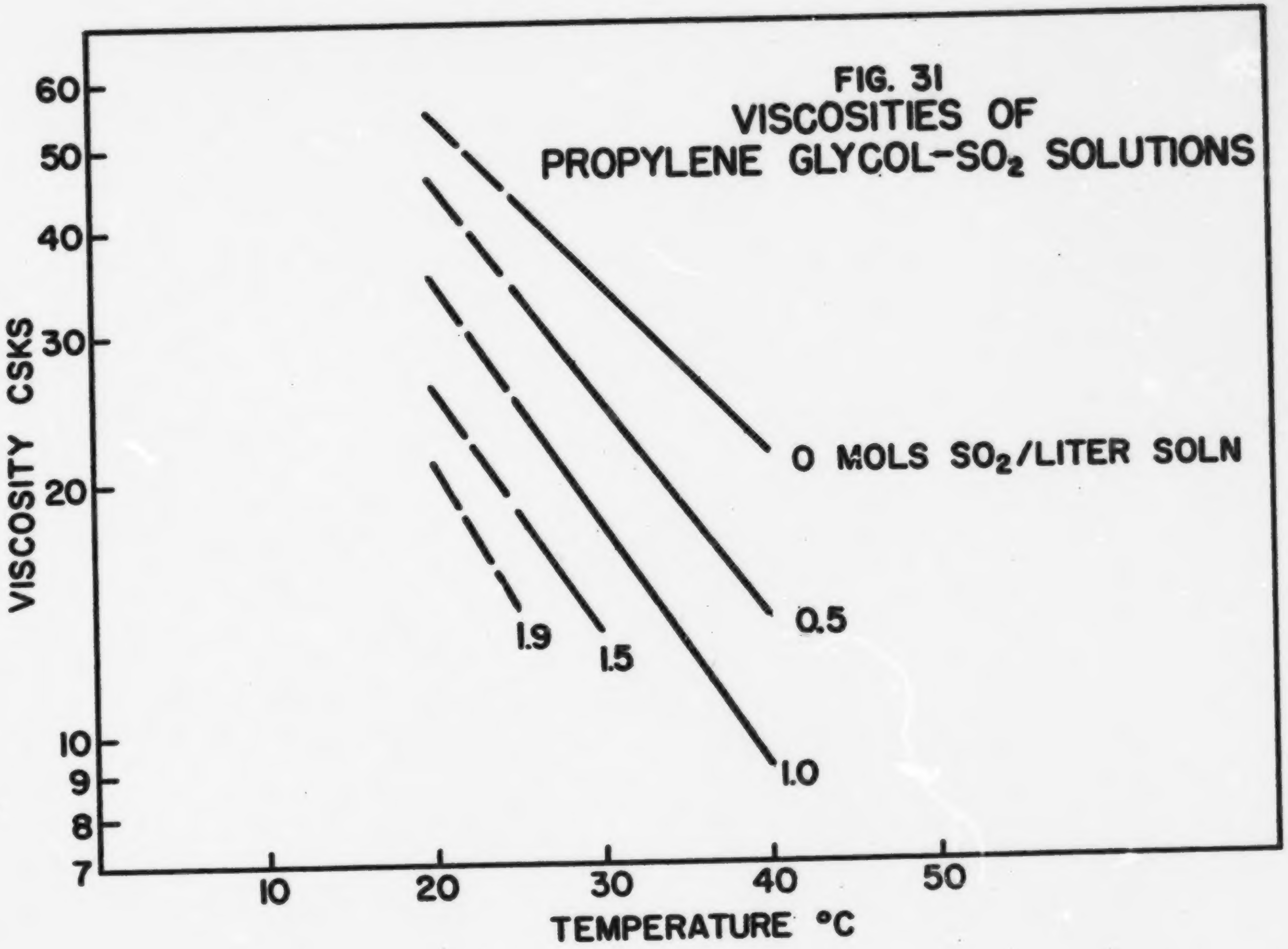

FIG. 31
VISCOSITIES OF
PROPYLENE GLYCOL-$SO_2$ SOLUTIONS

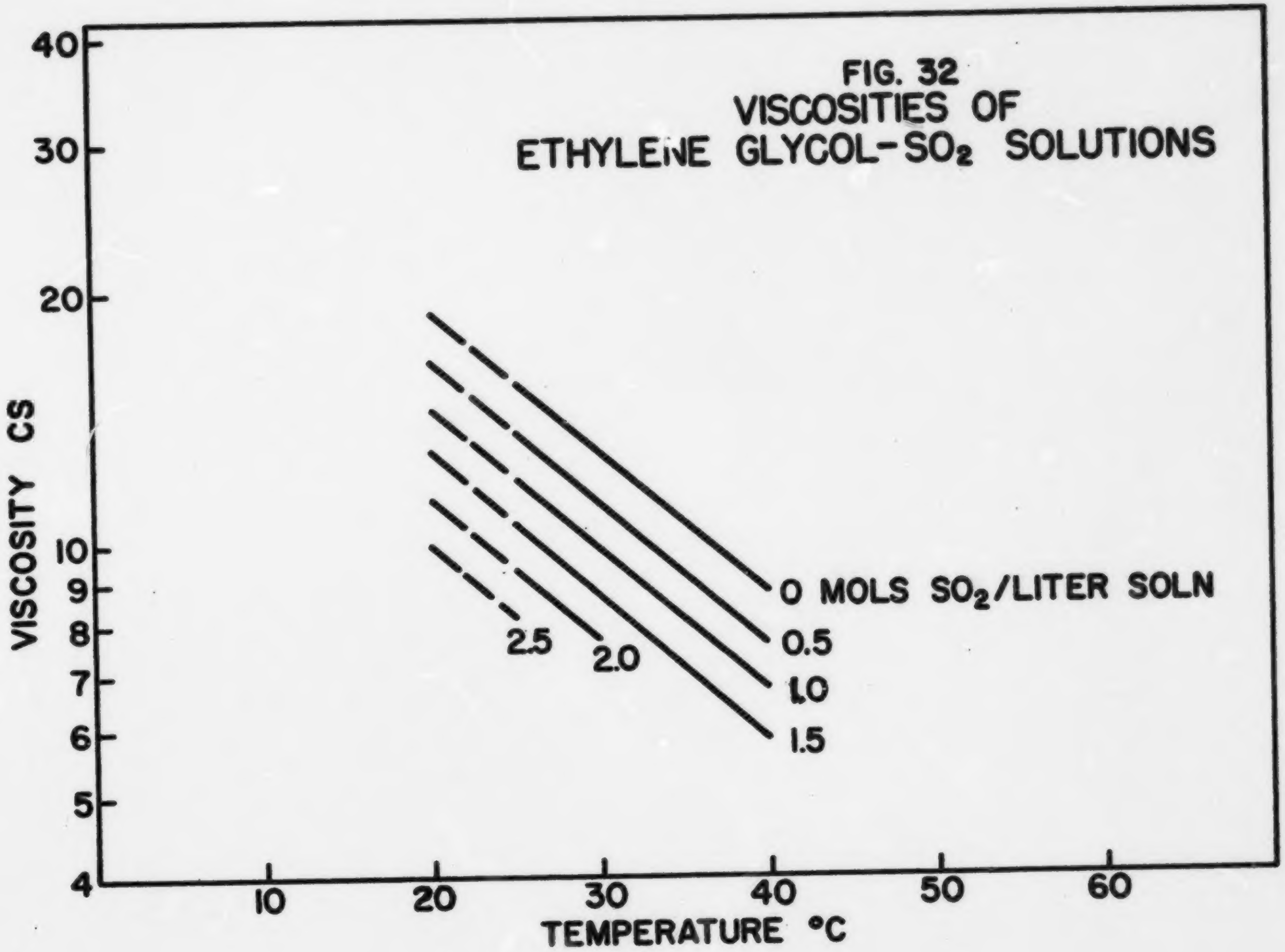

FIG. 32
VISCOSITIES OF
ETHYLENE GLYCOL-$SO_2$ SOLUTIONS

## TABLE 12

## DENSITIES OF $SO_2$ SOLUTIONS

| System | Ref. | Temp. | Conc. | Density |
|---|---|---|---|---|
| | | °C | $\frac{\text{mols SO}_2}{\text{liter soln.}}$ | $\frac{\text{gm.}}{\text{cm.}^3}$ |
| Glycerine-$SO_2$ | II- 74 | 25 | 0 | 1.2493 |
| | I-129 | 25 | 1.20 | 1.2693 |
| | II- 61 | 30 | 0 | 1.2461 |
| | II- 31 | 30 | 1.02 | 1.2633 |
| | II- 54 | 40 | 0 | 1.2410 |
| | II- 58 | 40 | 0.81 | 1.2533 |
| Propylene Glycol-$SO_2$ | II- 74 | 25 | 0 | 1.0337 |
| | II- 38 | 25 | 1.90 | 1.0915 |
| | II- 61 | 30 | 0 | 1.0303 |
| | II- 42 | 30 | 1.50 | 1.0752 |
| | II- 52 | 40 | 0 | 1.0236 |
| | II- 50 | 40 | 1.00 | 1.0521 |
| Ethylene Glycol-$SO_2$ | II- 77 | 25 | 0 | 1.1090 |
| | II- 4 | 25 | 2.65 | 1.1646 |
| | II- 61 | 30 | 0 | 1.1056 |
| | II- 26 | 30 | 2.25 | 1.1525 |
| | II- 52 | 40 | 0 | 1.0998 |
| | II- 53 | 40 | 1.60 | 1.1350 |

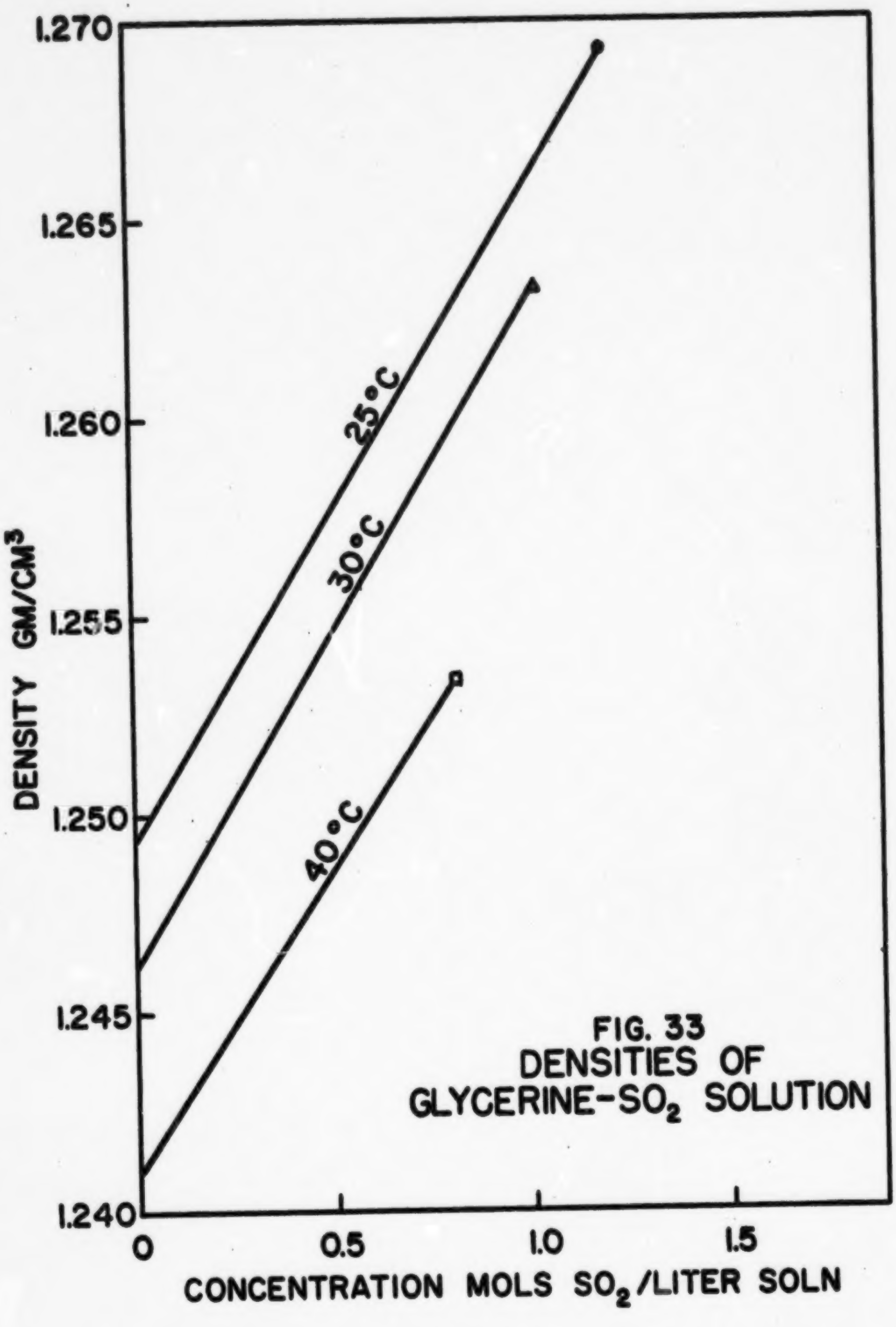

FIG. 33
DENSITIES OF
GLYCERINE-$SO_2$ SOLUTION

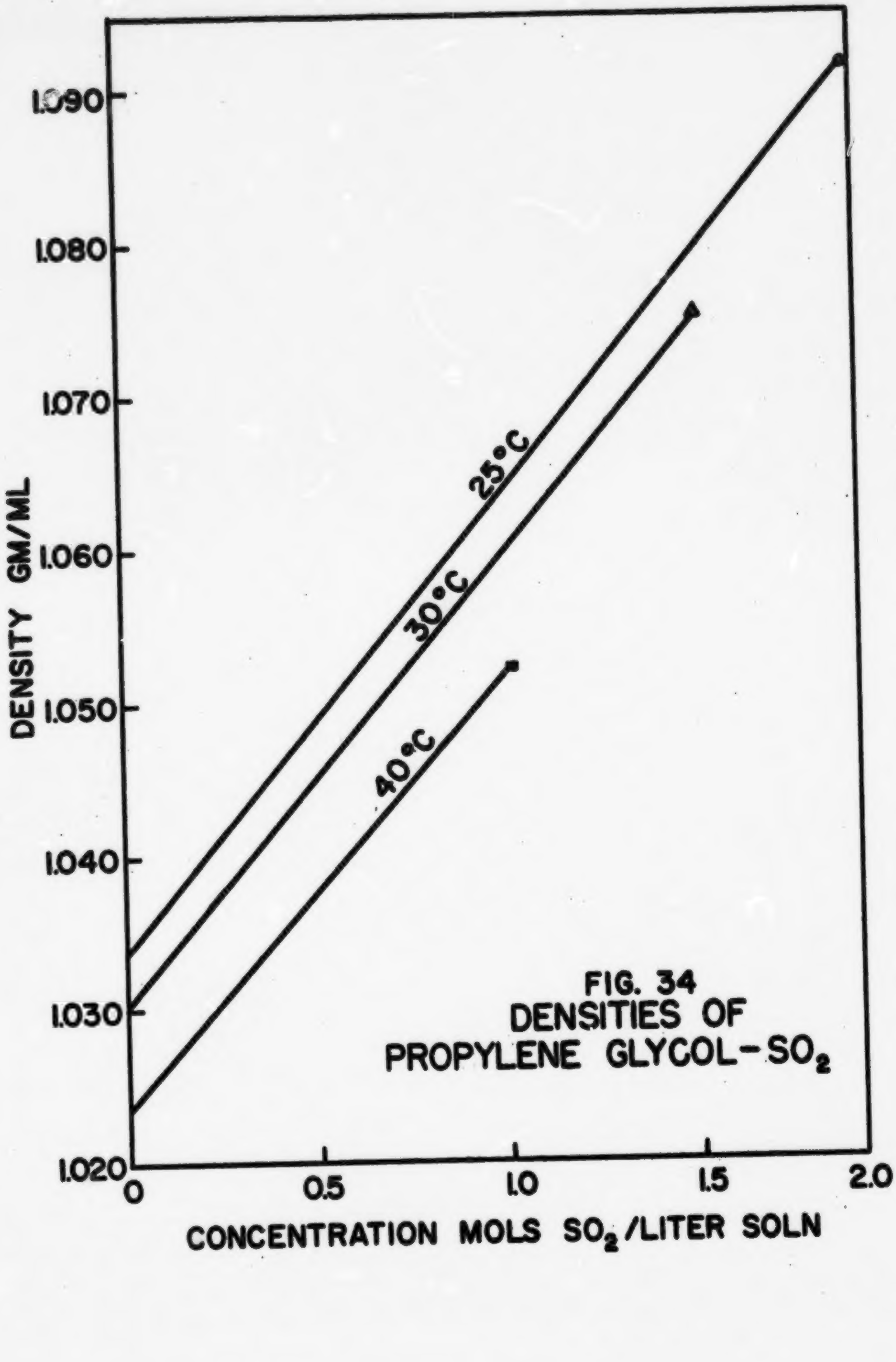

FIG. 34
DENSITIES OF
PROPYLENE GLYCOL-$SO_2$

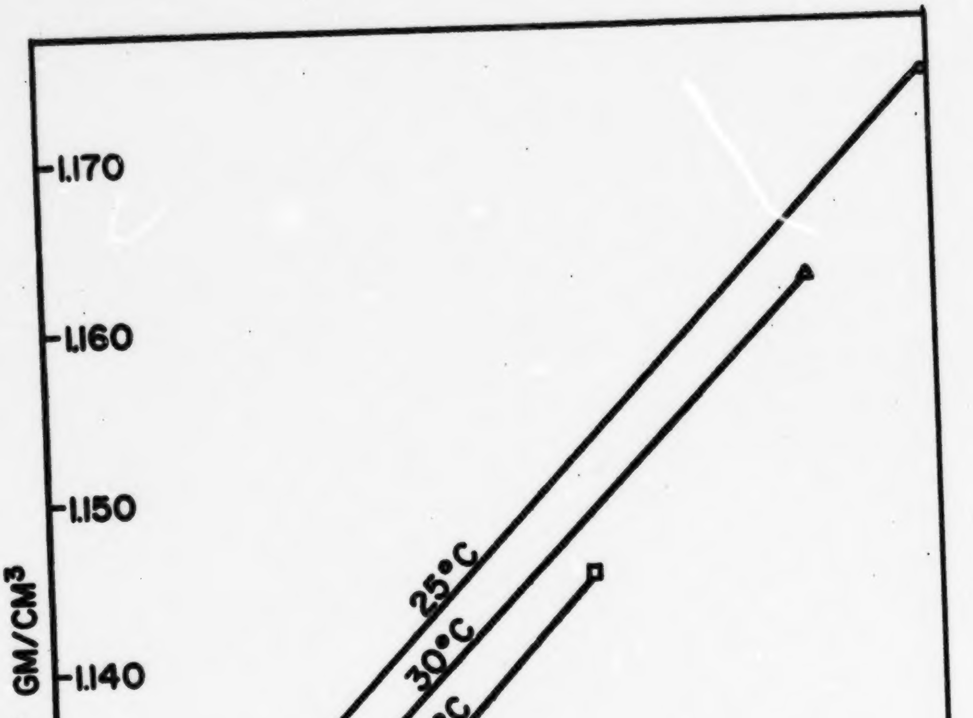

FIG. 35
DENSITIES OF
ETHYLENE GLYCOL-$SO_2$

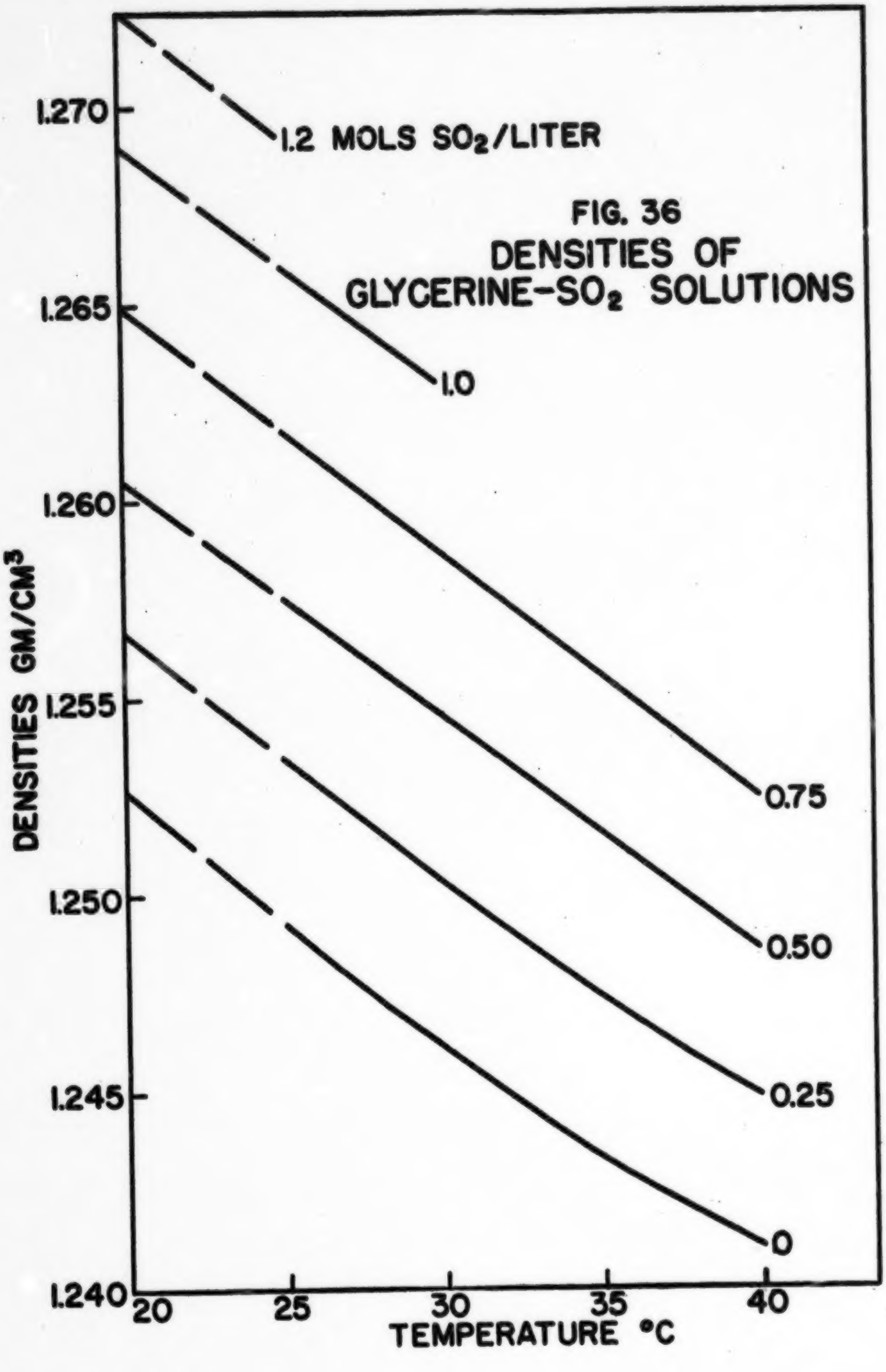

FIG. 36
DENSITIES OF
GLYCERINE-$SO_2$ SOLUTIONS

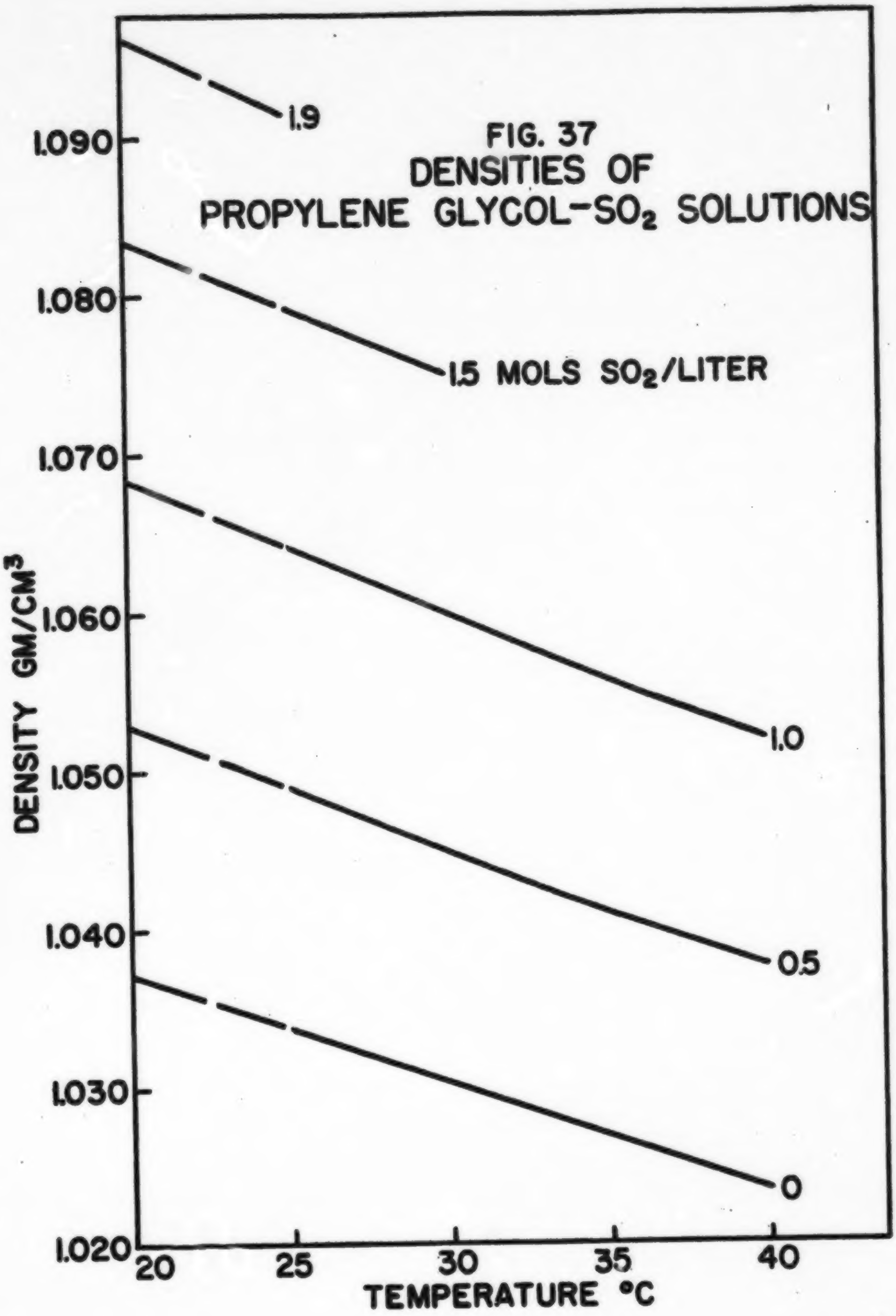

FIG. 37
DENSITIES OF
PROPYLENE GLYCOL-$SO_2$ SOLUTIONS

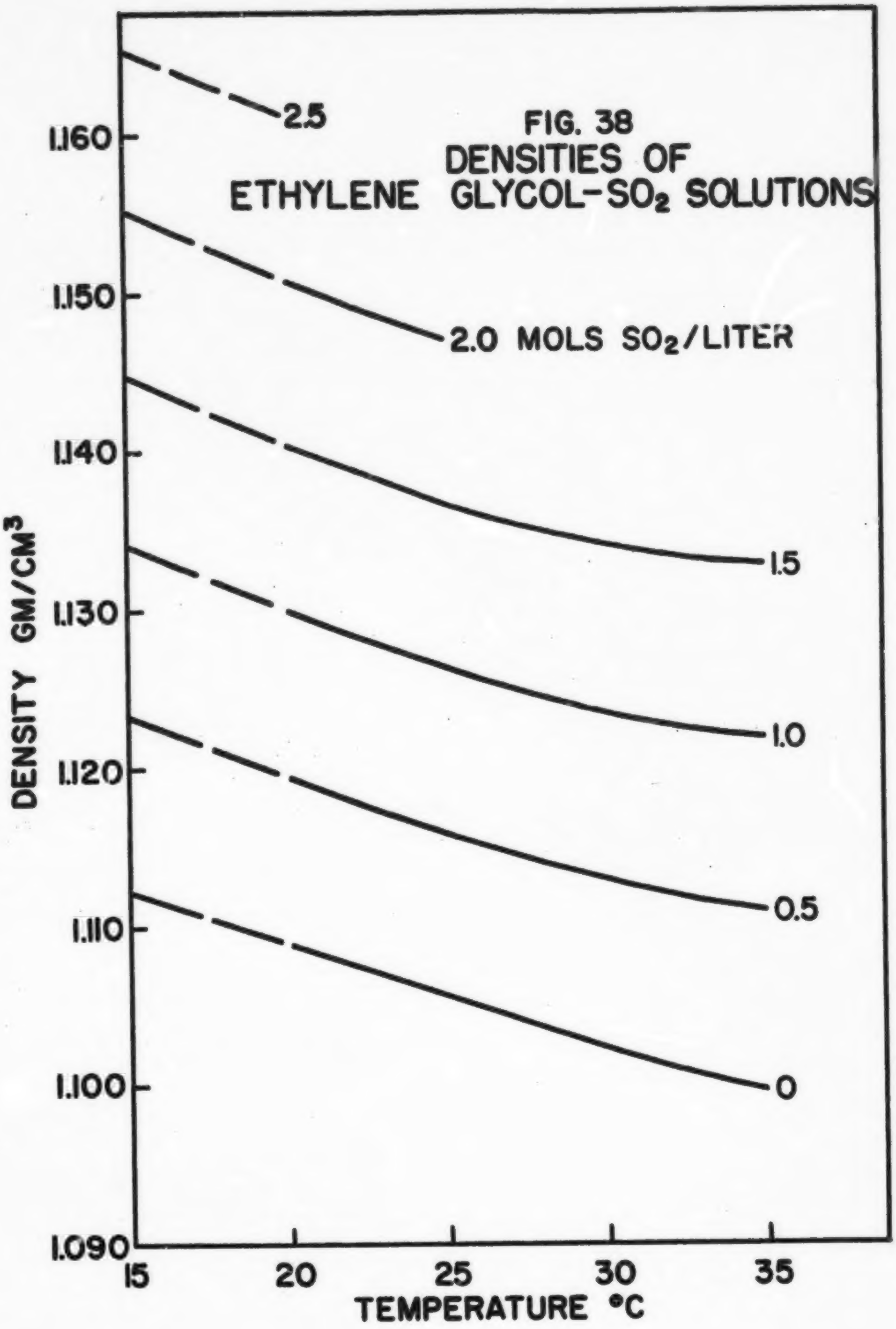
FIG. 38
DENSITIES OF
ETHYLENE GLYCOL-$SO_2$ SOLUTIONS
2.5
2.0 MOLS $SO_2$/LITER
1.5
1.0
0.5
0
DENSITY GM/CM$^3$
1.160
1.150
1.140
1.130
1.120
1.110
1.100
1.090
15
20
25
30
35
TEMPERATURE °C

## THEORETICAL DIFFUSIVITY CALCULATIONS

Using the Wilke-Chang method[38],

$$D_{12} = 7.4 \text{ X } 10^{-8} \frac{(\chi M)^{1/2} T}{\mu V_1^{0.6}}$$

$D_{12}$ = diffusion coefficient of solute 1 in dilute solution in solvent 2 at temp. T, $\frac{\text{cm.}^2}{\text{sec.}}$

M = mol. wt. of solvent

T = temperature, °K

$\mu$ = viscosity of solution, centipoises

$V_1$ = molal volume of solute at normal boiling point, $\frac{\text{cm.}^3}{\text{g. mol}}$

for $SO_2$ $V_1 = 43.8$

$\chi$ = "association" parameter of solvent

for unassociated solvents = 1. Assume it holds here.

$$\therefore D_{12} = 7.4 \text{ X } 10^{-8} \frac{(M)^{1/2} T}{\mu (43.8)^{0.6}} = 7.67 \text{ X } 10^{-9} \frac{M^{1/2} T}{\mu}$$

For Glycerine M = 92.09

$$D = 7.67 \text{ X } 10^{-9} (92.09)^{1/2} \frac{T}{\mu} = 7.32 \text{ X } 10^{-8} \frac{T}{\mu}$$

For Propylene Glycol M = 76.09

$$D = 7.67 \text{ X } 10^{-9} (76.09)^{1/2} \frac{T}{\mu} = 6.69 \text{ X } 10^{-8} \frac{T}{\mu}$$

For Ethylene Glycol M = 62.07

$$D = 7.67 \text{ X } 10^{-9} (67.07)^{1/2} \frac{T}{\mu} = 6.05 \text{ X } 10^{-8} \frac{T}{\mu}$$

The calculated values are plotted on Figures 9, 10, and 11.

# APPENDIX III

## ABSORPTION OF $SO_2$ BY OSCILLATING DROPS

### TABLE 13

### ABSORPTION OF $SO_2$ BY GLYCERINE DROPS

| Run | Support Diameter | Drop Volume | Gas Velocity | Temp. | Time | Final Conc. |
|---|---|---|---|---|---|---|
| | | | | | | N X $10^4$ |
| | in. | $cm.^3$ | $\frac{ft.}{sec}$ | °C | min. | |
| 1 | 0.028 | 0.0042 | 0 | 31.1 | 0.50 | 0.49 |
| 2 | 0.028 | 0.0042 | 0 | 31.1 | 1 | 0.845 |
| 3[(a)] | 0.028 | 0.0042 | 0 | . . . | . . . | . . . |
| 4 | 0.028 | 0.0042 | 0 | 31.5 | 1 | 0.89 |
| 5 | 0.028 | 0.0042 | 0 | 31.4 | 2 | 1.30 |
| 6 | 0.028 | 0.0042 | 0 | 31.2 | 8 | 3.18 |
| 7 | 0.028 | 0.0042 | 0 | 29.4 | 4 | 1.69 |
| 8 | 0.028 | 0.0042 | 0 | 30.4 | 16 | 4.33 |
| 9 | 0.028 | 0.0042 | 0 | 30.6 | 2 | 1.30 |
| 10 | 0.028 | 0.0042 | 0 | 30.7 | 3 | 1.38 |
| 11 | 0.028 | 0.0042 | 0 | 30.6 | 3 | 1.55 |
| 12 | 0.028 | 0.0042 | 0 | 30.5 | 3 | 1.42 |
| 13 | 0.028 | 0.0042 | 0 | 30.5 | 4 | 1.91 |
| 14 | 0.028 | 0.0042 | 0 | 30.3 | 5 | 1.90 |
| 15 | 0.028 | 0.0042 | 0 | 30.4 | 6 | 1.91 |
| 16 | 0.028 | 0.0042 | 0 | 28.0 | 12 | 3.10 |
| 17-19[(a)] | 0.028 | 0.0042 | 0 | . . . | . . . | . . . |
| 20 | 0.028 | 0.0042 | 0 | 28.0 | 2 | 0.690 |
| 21 | 0.028 | 0.0042 | 18.2 | 28.0 | 2 | 1.03 |
| 22 | 0.028 | 0.0042 | 18.2 | 28.0 | 2 | 0.88 |
| 23 | 0.028 | 0.0042 | 18.2 | 28.0 | 1 | 0.63 |
| 24 | 0.028 | 0.0042 | 18.2 | 28.0 | 3 | 0.94 |

TABLE 13—Continued

| $SO_2$ Absorbed | $c'_{sat.}$ | $\frac{c'}{c'_{sat.}}$ | $c_{avg.}$ | $D_{L_{avg.}}$ | $\frac{Dt}{a^2}$ |
|---|---|---|---|---|---|
| | | Final | | X $10^6$ | X $10^3$ |
| mols X $10^6$ | $\frac{\text{mols } SO_2}{\text{1000 gm. solvent}}$ | X 100 | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{\text{cm.}^2}{\text{sec.}}$ | |
| 0.306 | 0.854 | 6.8 | 0.495 | 1.18 | 0.35 |
| 0.528 | 0.854 | 11.7 | 0.495 | 1.18 | 0.71 |
| . . . | . . . | . . . | . . . | . . . | . . . |
| 0.556 | 0.815 | 12.9 | 0.488 | 1.22 | 0.73 |
| 0.812 | 0.818 | 18.7 | 0.490 | 1.21 | 1.45 |
| 1.99 | 0.824 | 45.4 | 0.492 | 1.19 | 5.72 |
| 1.06 | 0.870 | 22.9 | 0.518 | 1.03 | 2.47 |
| 2.71 | 0.818 | 62.5 | 0.502 | 1.12 | 10.75 |
| 0.812 | 0.812 | 18.8 | 0.499 | 1.14 | 1.37 |
| 0.862 | 0.809 | 20.0 | 0.498 | 1.15 | 2.07 |
| 0.968 | 0.812 | 22.5 | 0.499 | 1.14 | 2.05 |
| 0.887 | 0.815 | 20.5 | 0.501 | 1.13 | 2.03 |
| 1.19 | 0.815 | 27.5 | 0.501 | 1.13 | 2.74 |
| 1.19 | 0.821 | 27.3 | 0.503 | 1.11 | 3.33 |
| 1.19 | 0.818 | 27.4 | 0.502 | 1.12 | 4.03 |
| 1.94 | 0.915 | 39.8 | 0.543 | 0.91 | 6.55 |
| . . . | 0.915 | . . . | . . . | . . . | . . . |
| 0.431 | 0.915 | 8.8 | 0.543 | 0.91 | 1.09 |
| 0.644 | 0.915 | 13.2 | 0.543 | 0.91 | 1.09 |
| 0.551 | 0.915 | 11.3 | 0.543 | 0.91 | 1.09 |
| 0.394 | 0.915 | 8.1 | 0.543 | 0.91 | 0.546 |
| 0.588 | 0.915 | 12.1 | 0.543 | 0.91 | 1.64 |

TABLE 13—Continued

| Run | Support Diameter | Drop Volume | Gas Velocity | Temp. | Time | Final Conc. |
|---|---|---|---|---|---|---|
| | | | | | | N X $10^4$ |
| | in. | cm.$^3$ | $\frac{\text{ft.}}{\text{sec.}}$ | °C | min. | |
| 25 | 0.028 | 0.0042 | 26.8 | 28.5 | 1 | 0.68 |
| 26 | 0.028 | 0.0042 | 26.8 | 28.5 | 2 | 0.82 |
| 27 | 0.028 | 0.0042 | 26.8 | 28.5 | 3.25 | 1.27 |
| 28 | 0.028 | 0.0042 | 26.8 | 28.5 | 4 | 1.06 |
| 29 | 0.028 | 0.0042 | 26.8 | 28.5 | 5 | 1.71 |
| 30 | 0.028 | 0.0042 | 26.8 | 28.5 | 6 | 1.83 |
| 31 | 0.028 | 0.0042 | 26.8 | 28.5 | 7 | 2.14 |
| 32 | 0.028 | 0.0042 | 26.8 | 28.5 | 4 | 1.13 |
| 33-48(b) | 0.028 | 0.0042 | . . . | . . . | . . . | . . . |
| 49 | 0.028 | 0.0042 | 0 | 26.5 | 0.50 | 0.392 |
| 50(a) | 0.028 | 0.0042 | . . . | . . . | . . . | . . . |
| 51 | 0.028 | 0.0042 | 0 | 26.5 | 2 | 0.91 |
| 52 | 0.028 | 0.0042 | 0 | 26.5 | 4 | 1.85 |
| 53 | 0.028 | 0.0042 | 18.2 | 26.5 | 0.50 | 0.456 |
| 54 | 0.028 | 0.0042 | 18.2 | 26.5 | 1 | 1.10 |
| 55 | 0.028 | 0.0042 | 18.2 | 26.5 | 4 | 1.83 |
| 56 | 0.028 | 0.0042 | 18.2 | 26.5 | 2 | 1.62 |
| 57 | 0.028 | 0.0042 | 0 | 27.5 | 23 | 3.18 |
| 58 | 0.028 | 0.0042 | 0 | 27.5 | 13 | 2.82 |
| 59 | 0.028 | 0.0042 | 0 | 27.0 | 6 | 1.46 |
| 60 | 0.028 | 0.0042 | 0 | 26.5 | 3 | 1.16 |
| 61 | 0.028 | 0.0042 | 0 | 26.5 | 45 | 3.21 |
| 62 | 0.028 | 0.0042 | 0 | 26.5 | 21 | 2.65 |
| 63 | 0.028 | 0.0042 | 0 | 26.5 | 10 | 1.81 |
| 64 | 0.028 | 0.0042 | 0 | 26.5 | 5 | 0.86 |
| 65 | 0.028 | 0.0042 | 18.2 | 27.5 | 16 | 2.43 |
| 66 | 0.028 | 0.0042 | 18.2 | 28.0 | 8 | 2.43 |
| 67(a) | 0.028 | 0.0042 | . . . | . . . | . . . | . . . |
| 68 | 0.028 | 0.0042 | 18.2 | 28.0 | 2 | 1.71 |

Notes: (a) Handling losses during transfer.

(b) Malfunctioning of conductivity bridge.

TABLE 13—Continued

| $SO_2$ | $c'_{sat.}$ | $\frac{c'}{c'_{sat.}}$ | $c_{avg.}$ | $D_{L_{avg.}}$ | $\frac{Dt}{a^2}$ |
|---|---|---|---|---|---|
| | | Final | | X $10^6$ | X $10^3$ |
| mols X $10^6$ | $\frac{\text{mols } SO_2}{\text{1000 gm. solvent}}$ | X 100 | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{\text{cm.}^2}{\text{sec.}}$ | |
| 0.425 | 0.900 | 8.9 | 0.535 | 0.95 | 0.570 |
| 0.513 | 0.900 | 10.7 | 0.535 | 0.95 | 1.14 |
| 0.794 | 0.900 | 16.5 | 0.535 | 0.95 | 1.85 |
| 0.661 | 0.900 | 13.8 | 0.535 | 0.95 | 2.28 |
| 1.07 | 0.900 | 21.3 | 0.535 | 0.95 | 2.85 |
| 1.14 | 0.900 | 23.8 | 0.535 | 0.95 | 3.42 |
| 1.34 | 0.900 | 28.0 | 0.535 | 0.95 | 3.99 |
| 0.706 | 0.900 | 14.7 | 0.535 | 0.95 | 2.28 |
| . . . | . . . | . . . | . . . | . . . | . . . |
| 0.245 | 0.960 | 4.8 | 0.570 | 0.80 | 0.240 |
| . . . | . . . | . . . | . . . | . . . | . . . |
| 0.568 | 0.960 | 11.1 | 0.570 | 0.80 | 0.960 |
| 1.155 | 0.960 | 22.5 | 0.570 | 0.80 | 1.92 |
| 0.285 | 0.960 | 5.6 | 0.570 | 0.80 | 0.240 |
| 0.687 | 0.960 | 13.4 | 0.570 | 0.80 | 0.480 |
| 1.14 | 0.960 | 22.3 | 0.570 | 0.80 | 1.92 |
| 1.01 | 0.960 | 19.7 | 0.570 | 0.80 | 0.960 |
| 1.99 | 0.925 | 40.3 | 0.553 | 0.88 | 12.1 |
| 1.76 | 0.925 | 35.7 | 0.553 | 0.88 | 6.86 |
| 0.912 | 0.945 | 18.1 | 0.560 | 0.82 | 2.95 |
| 0.725 | 0.960 | 14.1 | 0.570 | 0.80 | 1.44 |
| 2.01 | 0.960 | 39.3 | 0.570 | 0.80 | 21.6 |
| 1.65 | 0.960 | 32.2 | 0.570 | 0.80 | 10.1 |
| 1.13 | 0.960 | 22.1 | 0.570 | 0.80 | 4.80 |
| 0.537 | 0.960 | 10.5 | 0.570 | 0.80 | 2.40 |
| 1.52 | 0.925 | 30.9 | 0.553 | 0.88 | 8.44 |
| 1.52 | 0.915 | 31.2 | 0.543 | 0.91 | 4.37 |
| . . . | . . . | . . . | . . . | . . . | . . . |
| 1.07 | 0.915 | 22.0 | 0.543 | 0.91 | 1.09 |

## TABLE 14

## ABSORPTION OF $SO_2$ BY PROPYLENE GLYCOL DROPS

| Run | Support Diameter | Drop Volume | Gas Velocity | Temp. | Time | Final Conc. |
|---|---|---|---|---|---|---|
| | | | | | | N X $10^3$ |
| | in. | $cm.^3$ | $\frac{ft.}{sec.}$ | °C | min. | |
| 1 | 0.037 | 0.0082 | 0 | 26.5 | 2 | 0.804 |
| 2 | 0.037 | 0.0082 | 0 | 26.0 | 4 | 1.06 |
| 3 | 0.037 | 0.0082 | 0 | 26.0 | 9 | 1.49 |
| 4 | 0.037 | 0.0082 | 0 | 26.0 | 17 | 1.81 |
| 5 | 0.037 | 0.0060 | 0 | 26.0 | 16 | 1.42 |
| 6 | 0.037 | 0.0060 | 0 | 26.0 | 8 | 1.12 |
| 7 | 0.037 | 0.0060 | 0 | 25.5 | 4 | 0.98 |
| 8 | 0.037 | 0.0060 | 0 | 25.5 | 2 | 0.785 |
| 9 | 0.037 | 0.0042 | 0 | 26.5 | 16 | 0.820 |
| 10 | 0.037 | 0.0042 | 0 | 26.5 | 8 | 0.690 |
| 11 | 0.037 | 0.0042 | 0 | 26.5 | 5 | 0.640 |
| 12 | 0.037 | 0.0042 | 0 | 26.5 | 2 | 0.551 |
| 13 | 0.037 | 0.0082 | 0 | 27.0 | 16 | 1.36 |
| 14 | 0.037 | 0.0082 | 0 | 27.5 | 9 | 1.15 |
| 15 | 0.037 | 0.0082 | 0 | 28.0 | 5.50 | 1.16 |
| 16 | 0.037 | 0.0082 | 0 | 28.5 | 2 | 1.01 |
| 17-24[(a)] | 0.037 | 0.0082 | . . . | . . . | . . . | . . . |
| 25 | 0.037 | 0.0082 | 18.2 | 26.5 | 4 | 1.43 |
| 26 | 0.037 | 0.0082 | 18.2 | 26.5 | 8 | 1.40 |
| 27 | 0.037 | 0.0082 | 18.2 | 28.0 | 16 | 1.49 |
| 28 | 0.037 | 0.0082 | 18.2 | 27.5 | 2 | 1.28 |
| 29 | 0.037 | 0.0042 | 18.2 | 28.5 | 2 | 0.645 |
| 30 | 0.037 | 0.0042 | 18.2 | 28.5 | 2 | 0.714 |
| 31 | 0.037 | 0.0042 | 18.2 | 29.0 | 8 | 0.714 |
| 32 | 0.037 | 0.0042 | 18.2 | 29.0 | 16 | 0.775 |
| 33 | 0.037 | 0.0042 | 0 | 27.5 | 16 | 0.735 |

TABLE 14—Continued

| $SO_2$ Absorbed | $c'_{sat.}$ | $\frac{c'}{c'_{sat.}}$ | $c_{avg.}$ | $D_{L\,avg.}$ | $\frac{Dt}{a^2}$ |
|---|---|---|---|---|---|
| | | Final | | X $10^6$ | X $10^3$ |
| mols X $10^6$ | $\frac{\text{mols } SO_2}{\text{1000 gm. solvent}}$ | X 100 | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{\text{cm.}^2}{\text{sec.}}$ | |
| 6.03 | 1.82 | 39.2 | 0.88 | 0.79 | 6.1 |
| 7.95 | 1.86 | 50.4 | 0.90 | 0.75 | 11.5 |
| 11.2 | 1.86 | 71.1 | 0.97 | 0.80 | 27.7 |
| 13.6 | 1.86 | 86.3 | 1.13 | 0.86 | 56.3 |
| 10.7 | 1.86 | 92.6 | 1.24 | 0.91 | 68.7 |
| 8.40 | 1.86 | 73.1 | 0.99 | 0.81 | 30.6 |
| 7.35 | 1.92 | 61.7 | 0.96 | 0.76 | 14.4 |
| 5.88 | 1.92 | 49.4 | 0.93 | 0.75 | 7.1 |
| 6.15 | 1.82 | 78.0 | 1.02 | 0.85 | 81.6 |
| 5.17 | 1.82 | 65.5 | 0.93 | 0.81 | 38.9 |
| 4.80 | 1.82 | 60.8 | 0.92 | 0.81 | 24.3 |
| 4.13 | 1.82 | 52.4 | 0.88 | 0.79 | 9.5 |
| 10.2 | 1.78 | 67.6 | 0.91 | 0.84 | 51.7 |
| 8.62 | 1.73 | 59.0 | 0.86 | 0.84 | 29.1 |
| 8.70 | 1.69 | 60.8 | 0.85 | 0.87 | 18.4 |
| 7.57 | 1.65 | 54.2 | 0.82 | 0.88 | 6.8 |
| . . . | . . . | . . . | . . . | . . . | . . . |
| 10.7 | 1.82 | 69.7 | 0.95 | 0.82 | 12.6 |
| 10.5 | 1.82 | 68.2 | 0.95 | 0.82 | 25.2 |
| 11.2 | 1.69 | 78.4 | 0.95 | 0.92 | 56.6 |
| 9.60 | 1.73 | 65.7 | 0.89 | 0.86 | 6.6 |
| 4.83 | 1.65 | 67.6 | 0.85 | 0.90 | 10.8 |
| 5.34 | 1.65 | 74.7 | 0.90 | 0.93 | 11.2 |
| 5.34 | 1.61 | 76.7 | 0.89 | 0.96 | 46.1 |
| 5.81 | 1.61 | 83.3 | 0.95 | 0.98 | 94.1 |
| 5.51 | 1.73 | 73.4 | 0.92 | 0.87 | 83.5 |

TABLE 14—Continued

| Run | Support Diameter | Drop Volume | Gas Velocity | Temp. | Time | Final Conc. |
|---|---|---|---|---|---|---|
| | | | | | | N X $10^3$ |
| | in. | cm.$^3$ | $\frac{\text{ft.}}{\text{sec.}}$ | °C | min. | |
| 34 | 0.037 | 0.0042 | 0 | 27.5 | 8 | 0.692 |
| 35 | 0.037 | 0.0042 | 0 | 27.5 | 4 | 0.591 |
| 36 | 0.037 | 0.0042 | 0 | 27.5 | 2 | 0.551 |
| 37 | 0.037 | 0.0060 | 0 | 27.5 | 2 | 0.780 |
| 38 | 0.037 | 0.0060 | 0 | 27.5 | 4 | 0.871 |
| 39 | 0.037 | 0.0060 | 0 | 27.0 | 16 | 0.980 |
| 40 | 0.037 | 0.0060 | 0 | 27.0 | 8 | 0.975 |
| 41 | 0.037 | 0.0082 | 0 | 26.0 | 16 | 1.43 |
| 42 | 0.037 | 0.0082 | 0 | 26.0 | 8 | 1.25 |
| 43 | 0.037 | 0.0082 | 0 | 26.0 | 4 | 1.11 |
| 44 | 0.037 | 0.0082 | 0 | 26.5 | 2 | 1.04 |
| 45 | 0.037 | 0.0082 | 0 | 28.0 | 1 | 0.820 |
| 46 | 0.037 | 0.0082 | 0 | 28.0 | 0.55 | 0.808 |
| 47 | 0.037 | 0.0082 | 0 | 28.0 | 0.28 | 0.655 |
| 48 | 0.037 | 0.0082 | 0 | 28.0 | 1.03 | 0.811 |
| 49 | 0.037 | 0.0110 | 0 | 28.0 | 1 | 1.15 |
| 50 | 0.037 | 0.0110 | 0 | 28.0 | 0.50 | 0.850 |
| 51 | 0.037 | 0.0110 | 0 | 27.5 | 0.28 | 0.810 |
| 52 | 0.037 | 0.0110 | 0 | 27.5 | 2 | 1.12 |
| 53 | 0.037 | 0.0082 | 18.2 | 30.5 | 1.05 | 1.04 |
| 54 | 0.037 | 0.0082 | 18.2 | 30.5 | 0.53 | 0.910 |
| 55 | 0.037 | 0.0082 | 18.2 | 30.5 | 2 | 1.06 |
| 56 | 0.037 | 0.0082 | 18.2 | 30.5 | 4.08 | 1.13 |
| 57 | 0.037 | 0.0082 | 10.0 | 30.5 | 0.53 | 0.896 |
| 58 | 0.037 | 0.0082 | 10.0 | 30.5 | 1.05 | 1.10 |
| 59 | 0.037 | 0.0082 | 10.0 | 30.5 | 2.08 | 1.07 |
| 60(b) | . . . | . . . | . . . | . . . | . . . | . . . |
| 61 | 0.037 | 0.0082 | 13.9 | 32.0 | 4.05 | 1.14 |
| 62 | 0.037 | 0.0082 | 13.9 | 32.0 | 2.07 | 1.09 |
| 63 | 0.037 | 0.0082 | 13.9 | 32.0 | 1.03 | 1.04 |
| 64 | 0.037 | 0.0082 | 13.9 | 32.0 | 0.53 | 0.970 |
| 65 | 0.037 | 0.0082 | 22.4 | 32.0 | 4.03 | 1.15 |
| 66 | 0.037 | 0.0082 | 22.4 | 32.0 | 2.07 | 1.11 |
| 67 | 0.037 | 0.0082 | 22.4 | 32.0 | 1.02 | 1.04 |
| 68 | 0.037 | 0.0082 | 22.4 | 32.0 | 0.55 | 0.960 |

TABLE 14—Continued

| $SO_2$ Absorbed | $c'_{sat.}$ | $\frac{c'}{c'_{sat.}}$ | $c_{avg.}$ | $D_{L\,avg.}$ | $\frac{Dt}{a^2}$ |
|---|---|---|---|---|---|
| | | Final | | X $10^6$ | X $10^3$ |
| mols X $10^6$ | $\frac{\text{mols } SO_2}{\text{1000 gm. solvent}}$ | X 100 | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{\text{cm.}^2}{\text{sec.}}$ | |
| 5.19 | 1.73 | 69.2 | 0.91 | 0.87 | 41.8 |
| 4.43 | 1.73 | 59.1 | 0.86 | 0.84 | 20.2 |
| 4.13 | 1.73 | 55.1 | 0.87 | 0.85 | 10.2 |
| 5.85 | 1.73 | 54.7 | 0.86 | 0.84 | 7.9 |
| 6.53 | 1.73 | 61.1 | 0.87 | 0.85 | 16.1 |
| 7.35 | 1.78 | 66.8 | 0.91 | 0.86 | 64.9 |
| 7.32 | 1.78 | 66.6 | 0.91 | 0.86 | 32.5 |
| 10.7 | 1.86 | 68.0 | 0.95 | 0.79 | 48.6 |
| 9.37 | 1.86 | 59.5 | 0.92 | 0.78 | 24.0 |
| 8.32 | 1.86 | 52.9 | 0.92 | 0.78 | 12.0 |
| 7.80 | 1.82 | 50.7 | 0.88 | 0.79 | 6.1 |
| 6.15 | 1.69 | 43.1 | 0.82 | 0.86 | 3.3 |
| 6.06 | 1.69 | 42.4 | 0.82 | 0.86 | 1.82 |
| 4.91 | 1.69 | 34.4 | 0.82 | 0.86 | 0.77 |
| 6.09 | 1.69 | 42.6 | 0.82 | 0.86 | 2.82 |
| 8.62 | 1.69 | 45.0 | 0.82 | 0.86 | 2.73 |
| 6.37 | 1.69 | 33.2 | 0.82 | 0.86 | 1.37 |
| 6.07 | 1.73 | 31.0 | 0.84 | 0.83 | 0.746 |
| 8.40 | 1.73 | 42.8 | 0.84 | 0.83 | 5.27 |
| 7.80 | 1.50 | 61.6 | 0.76 | 0.97 | 3.91 |
| 6.82 | 1.50 | 53.9 | 0.74 | 0.96 | 1.97 |
| 8.95 | 1.50 | 70.8 | 0.79 | 0.99 | 7.6 |
| 8.47 | 1.50 | 67.0 | 0.77 | 0.98 | 15.4 |
| 6.72 | 1.50 | 53.1 | 0.74 | 0.96 | 1.97 |
| 8.25 | 1.50 | 65.2 | 0.76 | 0.97 | 3.91 |
| 8.02 | 1.50 | 63.3 | 0.76 | 0.97 | 7.8 |
| . . . | . . . | . . . | . . . | . . . | . . . |
| 8.55 | 1.40 | 72.4 | 0.75 | 1.08 | 16.8 |
| 8.18 | 1.40 | 69.3 | 0.73 | 1.06 | 7.8 |
| 7.80 | 1.40 | 66.1 | 0.72 | 1.05 | 4.2 |
| 7.27 | 1.40 | 61.6 | 0.70 | 1.04 | 2.13 |
| 8.62 | 1.40 | 73.0 | 0.74 | 1.07 | 16.6 |
| 8.32 | 1.40 | 70.5 | 0.73 | 1.06 | 8.4 |
| 7.80 | 1.40 | 66.1 | 0.72 | 1.05 | 4.1 |
| 7.20 | 1.40 | 61.0 | 0.70 | 1.04 | 2.20 |

TABLE 14—Continued

| Run | Support Diameter | Drop Volume | Gas Velocity | Temp. | Time | Final Conc. |
|---|---|---|---|---|---|---|
| | | | | | | $N \times 10^3$ |
| | in. | $cm.^3$ | $\frac{ft.}{sec.}$ | °C | min. | |
| 69[a] | . . . | . . . | . . . | . . . | . . . | . . . |
| 70 | 0.028 | 0.0082 | 18.2 | 26.5 | 1.03 | 1.16 |
| 71 | 0.028 | 0.0082 | 18.2 | 26.5 | 11 | 1.45 |
| 72 | 0.028 | 0.0082 | 18.2 | 26.5 | 4.08 | 1.29 |
| 73-76[c] | 0.017 | 0.0042 | 18.2 | 26.5 | . . . | . . . |

Notes: (a) Low gas analysis.

(b) Handling losses during transfer.

(c) Element too small to support drops.

TABLE 14—Continued

| $SO_2$ Absorbed | $c'_{sat.}$ | $\frac{c'}{c'_{sat.}}$ | $c_{avg.}$ | $D_{L_{avg.}}$ | $\frac{Dt}{a^2}$ |
|---|---|---|---|---|---|
| | | Final | | $X\ 10^6$ | $X\ 10^3$ |
| mols $X\ 10^6$ | $\frac{\text{mols } SO_2}{\text{1000 gm. solvent}}$ | X 100 | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{\text{cm.}^2}{\text{sec.}}$ | |
| . . . | . . . | . . . | . . . | . . . | . . . |
| 8.70 | 1.82 | 56.5 | 0.90 | 0.80 | 3.18 |
| 10.9 | 1.82 | 70.8 | 0.95 | 0.82 | 34.7 |
| 9.68 | 1.82 | 62.8 | 0.92 | 0.81 | 12.7 |
| . . . | . . . | . . . | . . . | . . . | . . . |

## TABLE 15

## ABSORPTION OF $SO_2$ BY ETHYLENE GLYCOL DROPS

| Run | Support Diameter | Drop Volume | Gas Velocity | Temp. | Time | Final Conc. |
|---|---|---|---|---|---|---|
|  |  |  |  |  |  | $N \times 10^3$ |
|  | in. | $cm.^3$ | ft./sec. | °C | min. |  |
| 1-37(a) | . . . | . . . | . . . | . . . | . . . | . . . |
| 38 | 0.028 | 0.0082 | 0 | 26.0 | 20 | 2.12 |
| 39 | 0.028 | 0.0082 | 0 | 26.0 | 10 | 1.78 |
| 40 | 0.028 | 0.0082 | 0 | 26.0 | 5 | 1.35 |
| 41 | 0.028 | 0.0082 | 0 | 26.0 | 2.5 | 1.17 |
| 42 | 0.028 | 0.0082 | 18.2 | 26.5 | 2.5 | 1.51 |
| 43 | 0.028 | 0.0082 | 18.2 | 26.5 | 5 | 1.66 |
| 44 | 0.028 | 0.0082 | 18.2 | 27.0 | 10 | 2.00 |
| 45 | 0.028 | 0.0082 | 18.2 | 27.5 | 20 | 2.30 |
| 46 | 0.028 | 0.0042 | 0 | 27.5 | 2 | 0.534 |
| 47 | 0.028 | 0.0042 | 0 | 27.5 | 4 | 0.688 |
| 48 | 0.028 | 0.0042 | 0 | 27.5 | 8 | 0.824 |
| 49 | 0.028 | 0.0042 | 0 | 27.5 | 16 | 1.00 |
| 50 | 0.028 | 0.0042 | 18.2 | 27.5 | 2 | 0.689 |
| 51 | 0.028 | 0.0042 | 18.2 | 27.5 | 4 | 0.771 |
| 52 | 0.028 | 0.0042 | 18.2 | 28.0 | 8 | 0.944 |
| 53 | 0.028 | 0.0042 | 18.2 | 28.0 | 16 | 1.01 |
| 54 | 0.028 | 0.0060 | 0 | 28.0 | 2 | 0.764 |
| 55 | 0.028 | 0.0060 | 0 | 28.0 | 4 | 0.938 |
| 56 | 0.028 | 0.0060 | 0 | 28.0 | 8 | 1.11 |
| 57 | 0.028 | 0.0060 | 0 | 28.0 | 16 | 1.20 |
| 58 | 0.028 | 0.0060 | 18.2 | 28.0 | 2 | 0.99 |
| 59 | 0.028 | 0.0060 | 18.2 | 28.0 | 4 | 1.14 |
| 60 | 0.028 | 0.0060 | 18.2 | 28.5 | 8 | 1.33 |
| 61 | 0.028 | 0.0060 | 18.2 | 28.5 | 16 | 1.48 |
| 62 | 0.028 | 0.0082 | 0 | 25.5 | 16 | 1.97 |
| 63 | 0.028 | 0.0082 | 0 | 25.5 | 8 | 1.56 |
| 64 | 0.028 | 0.0082 | 0 | 25.5 | 5 | 1.30 |
| 65 | 0.028 | 0.0082 | 0 | 25.5 | 2 | 1.11 |
| 66 | 0.028 | 0.0082 | 10.0 | 26.0 | 2 | 1.43 |
| 67 | 0.028 | 0.0082 | 10.0 | 26.0 | 4 | 1.56 |
| 68 | 0.028 | 0.0082 | 10.0 | 26.0 | 16 | 2.12 |
| 69 | 0.028 | 0.0082 | 10.0 | 26.0 | 8 | 1.93 |

### TABLE 15—Continued

| $SO_2$ Absorbed | $c'_{sat.}$ | $\frac{c'}{c'_{sat.}}$ | $c_{avg.}$ | $D_{L_{avg.}}$ | $\frac{Dt}{a^2}$ |
|---|---|---|---|---|---|
| | | Final | | X $10^6$ | |
| mols X $10^6$ | $\frac{\text{mols } SO_2}{\text{1000 gm. Solvent}}$ | X 100 | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{cm.^2}{sec.}$ | |
| . . . | . . . | . . . | . . . | . . . | . . . |
| 15.9 | 2.59 | 64.3 | 1.36 | 1.51 | 0.116 |
| 13.4 | 2.59 | 54.0 | 1.31 | 1.49 | .0573 |
| 10.1 | 2.59 | 41.0 | 1.28 | 1.48 | .0285 |
| 8.77 | 2.59 | 35.5 | 1.28 | 1.48 | .0142 |
| 11.3 | 2.54 | 46.8 | 1.26 | 1.51 | .0145 |
| 12.4 | 2.54 | 51.5 | 1.26 | 1.51 | .0291 |
| 15.0 | 2.50 | 63.0 | 1.29 | 1.56 | .0581 |
| 17.3 | 2.45 | 75.0 | 1.37 | 1.62 | .115 |
| 4.01 | 2.45 | 33.6 | 1.22 | 1.57 | .0189 |
| 5.16 | 2.45 | 43.3 | 1.22 | 1.57 | .0373 |
| 6.18 | 2.45 | 52.0 | 1.22 | 1.57 | .0754 |
| 7.50 | 2.45 | 63.0 | 1.27 | 1.59 | .153 |
| 5.17 | 2.45 | 43.4 | 1.22 | 1.57 | .0189 |
| 5.78 | 2.45 | 48.6 | 1.22 | 1.57 | .0373 |
| 7.08 | 2.40 | 60.8 | 1.26 | 1.61 | .0773 |
| 7.57 | 2.40 | 65.0 | 1.28 | 1.62 | .152 |
| 5.73 | 2.40 | 34.4 | 1.21 | 1.60 | .0151 |
| 7.03 | 2.40 | 42.2 | 1.21 | 1.60 | .0302 |
| 8.32 | 2.40 | 50.0 | 1.21 | 1.60 | .0605 |
| 9.04 | 2.40 | 54.2 | 1.23 | 1.60 | .121 |
| 7.42 | 2.40 | 44.6 | 1.21 | 1.60 | .0151 |
| 8.55 | 2.40 | 51.3 | 1.21 | 1.60 | .0302 |
| 9.97 | 2.36 | 60.7 | 1.23 | 1.64 | .0620 |
| 11.0 | 2.36 | 67.0 | 1.25 | 1.65 | .125 |
| 14.8 | 2.64 | 58.7 | 1.20 | 1.42 | .0873 |
| 11.7 | 2.64 | 46.5 | 1.30 | 1.46 | .0450 |
| 9.78 | 2.64 | 38.9 | 1.30 | 1.46 | .0281 |
| 8.32 | 2.64 | 33.1 | 1.30 | 1.46 | .0112 |
| 10.7 | 2.59 | 43.4 | 1.28 | 1.48 | .0114 |
| 11.7 | 2.59 | 47.4 | 1.28 | 1.48 | .0228 |
| 15.9 | 2.59 | 64.4 | 1.36 | 1.51 | .0930 |
| 14.5 | 2.59 | 58.6 | 1.31 | 1.49 | 0.0458 |

TABLE 15—Continued

| Run | Support Diameter | Drop Volume | Gas Velocity | Temp. | Time | Final Conc. |
|---|---|---|---|---|---|---|
| | | | | | | $N \times 10^3$ |
| | in. | $cm.^3$ | $\frac{ft.}{sec.}$ | °C | min. | |
| 70 | 0.028 | 0.0082 | 22.4 | 26.0 | 16 | 2.25 |
| 71 | 0.028 | 0.0082 | 22.4 | 26.0 | 8 | 1.95 |
| 72 | 0.028 | 0.0082 | 22.4 | 26.0 | 4 | 1.68 |
| 73 | 0.028 | 0.0082 | 22.4 | 26.0 | 2 | 1.46 |
| 74 | 0.028 | 0.0082 | 13.9 | 26.5 | 2 | 1.36 |
| 75 | 0.028 | 0.0082 | 13.9 | 27.0 | 4 | 1.81 |
| 76 | 0.028 | 0.0082 | 13.9 | 27.0 | 8 | 1.81 |
| 77 | 0.028 | 0.0082 | 13.9 | 27.0 | 16 | 2.10 |
| 78 | 0.037 | 0.0082 | 18.2 | 25.0 | 16 | 2.32 |
| 79 | 0.037 | 0.0082 | 18.2 | 25.0 | 8 | 2.00 |
| 80 | 0.037 | 0.0082 | 18.2 | 24.5 | 4 | 1.75 |
| 81 | 0.037 | 0.0082 | 18.2 | 24.5 | 2 | 1.51 |
| 82 | 0.037 | 0.0082 | 10.0 | 24.5 | 2 | 1.45 |
| 83 | 0.037 | 0.0082 | 10.0 | 24.5 | 4 | 1.69 |
| 84 | 0.037 | 0.0082 | 10.0 | 24.5 | 8 | 1.95 |
| 85 | 0.037 | 0.0082 | 10.0 | 24.0 | 16 | 2.26 |

Note: (a) Low gas analyses and handling losses.

TABLE 15—Continued

| $SO_2$ Absorbed | $c'_{sat.}$ | $\frac{c'}{c'_{sat.}}$ | $c_{avg.}$ | $D_{L_{avg.}}$ | $\frac{Dt}{a^2}$ |
|---|---|---|---|---|---|
| | | Final | | X $10^6$ | |
| mols X $10^6$ | $\frac{\text{mols } SO_2}{\text{1000 gm. Solvent}}$ | X 100 | $\frac{\text{mols } SO_2}{\text{liter soln.}}$ | $\frac{\text{cm.}^2}{\text{sec.}}$ | |
| 16.9 | 2.59 | 68.4 | 1.38 | 1.51 | 0.0930 |
| 14.6 | 2.59 | 58.3 | 1.31 | 1.49 | .0458 |
| 12.6 | 2.59 | 51.1 | 1.28 | 1.48 | .0228 |
| 11.0 | 2.59 | 44.4 | 1.28 | 1.48 | .0114 |
| 10.2 | 2.54 | 42.2 | 1.26 | 1.51 | .0116 |
| 13.6 | 2.50 | 57.1 | 1.27 | 1.53 | .0237 |
| 13.6 | 2.50 | 57.1 | 1.27 | 1.53 | .0471 |
| 15.8 | 2.50 | 66.2 | 1.32 | 1.54 | .0948 |
| 17.4 | 2.69 | 67.7 | 1.41 | 1.46 | .0898 |
| 15.0 | 2.69 | 58.3 | 1.35 | 1.44 | .0443 |
| 13.1 | 2.73 | 50.4 | 1.35 | 1.41 | .0217 |
| 11.3 | 2.73 | 43.4 | 1.35 | 1.41 | .0108 |
| 10.9 | 2.73 | 41.8 | 1.35 | 1.41 | .0108 |
| 12.7 | 2.73 | 48.7 | 1.35 | 1.41 | .0217 |
| 14.6 | 2.73 | 56.1 | 1.38 | 1.41 | .0434 |
| 17.0 | 2.78 | 63.9 | 1.45 | 1.41 | 0.0867 |

## TABLE 16

## ETHYLENE GLYCOL-$SO_2$ DROPS , DROP SIZE VARIABLE

**Support Element Diameter = 0.028 inches**

| Run | Drop Size | Velocity | $\frac{D\theta}{a^2}$ | % Satn. |
|---|---|---|---|---|
| | $cm.^3$ | $\frac{ft.}{sec.}$ | | |
| 46 | 0.0042 | 0 | 0.0189 | 33.6 |
| 47 | .0042 | 0 | .0373 | 43.3 |
| 48 | .0042 | 0 | .0754 | 52.0 |
| 49 | .0042 | 0 | .1525 | 63.0 |
| 50 | .0042 | 18.2 | .0189 | 43.4 |
| 51 | .0042 | 18.2 | .0373 | 48.6 |
| 52 | .0042 | 18.2 | .0773 | 60.8 |
| 53 | .0042 | 18.2 | .1515 | 65.0 |
| 54 | .0060 | 0 | .0151 | 34.4 |
| 55 | .0060 | 0 | .0302 | 42.2 |
| 56 | .0060 | 0 | .0605 | 50.0 |
| 57 | .0060 | 0 | .1210 | 54.2 |
| 58 | .0060 | 18.2 | .0151 | 44.6 |
| 59 | .0060 | 18.2 | .0302 | 51.3 |
| 60 | .0060 | 18.2 | .0620 | 60.7 |
| 61 | .0060 | 18.2 | .1246 | 67.0 |
| 38 | .0082 | 0 | .1162 | 64.3 |
| 39 | .0082 | 0 | .0573 | 54.0 |
| 40 | .0082 | 0 | .0285 | 41.0 |
| 41 | .0082 | 0 | .0142 | 35.5 |
| 62 | .0082 | 0 | .0873 | 58.7 |
| 63 | .0082 | 0 | .0450 | 46.5 |
| 64 | .0082 | 0 | .0281 | 38.9 |
| 65 | .0082 | 0 | .0112 | 33.1 |
| 42 | .0082 | 18.2 | .0145 | 46.8 |
| 43 | .0082 | 18.2 | .0291 | 51.5 |
| 44 | .0082 | 18.2 | .0581 | 63.0 |
| 45 | 0.0082 | 18.2 | 0.1152 | 75.0 |

## TABLE 17

## ETHYLENE GLYCOL-$SO_2$ DROPS , SUPPORT ELEMENT VARIATION

| Element Diameter | Run | Drop | Velocity | $\frac{Dt}{a^2}$ | % Satn. |
|---|---|---|---|---|---|
| inches | | ml. | $\frac{ft.}{sec.}$ | | |
| 0.028 | 66 | 0.0082 | 10.0 | 0.0114 | 43.4 |
| 0.028 | 67 | .0082 | 10.0 | .0228 | 47.4 |
| 0.028 | 68 | .0082 | 10.0 | .0930 | 64.4 |
| 0.028 | 69 | .0082 | 10.0 | .0458 | 58.6 |
| 0.028 | 42 | .0082 | 18.2 | .0145 | 46.8 |
| 0.028 | 43 | .0082 | 18.2 | .0291 | 51.5 |
| 0.028 | 44 | .0082 | 18.2 | .0581 | 63.0 |
| 0.028 | 45 | .0082 | 18.2 | .1152 | 75.0 |
| 0.037 | 82 | .0082 | 10.0 | .0108 | 41.8 |
| 0.037 | 83 | .0082 | 10.0 | .0217 | 48.7 |
| 0.037 | 84 | .0082 | 10.0 | .0434 | 56.1 |
| 0.037 | 85 | .0082 | 10.0 | .0867 | 63.9 |
| 0.037 | 78 | .0082 | 18.2 | .0898 | 67.7 |
| 0.037 | 79 | .0082 | 18.2 | .0443 | 58.3 |
| 0.037 | 80 | .0082 | 18.2 | .0217 | 50.4 |
| 0.037 | 81 | 0.0082 | 18.2 | 0.0108 | 43.4 |

## TABLE 18

## ETHYLENE GLYCOL-$SO_2$ DROPS , VELOCITY VARIABLE

Drop size = 0.0082 cm.$^3$

Support Element Diameter = 0.028 inches

| Run | Velocity | $\frac{D\theta}{a^2}$ | % Satn. |
|---|---|---|---|
| | $\frac{ft.}{sec.}$ | | |
| 38 | 0 | 0.1162 | 64.3 |
| 39 | 0 | .0573 | 54.0 |
| 40 | 0 | .0285 | 41.0 |
| 41 | 0 | .0142 | 35.5 |
| 62 | 0 | .0873 | 58.7 |
| 63 | 0 | .0450 | 46.5 |
| 64 | 0 | .0281 | 38.9 |
| 65 | 0 | .0112 | 33.1 |
| 66 | 10.0 | .0114 | 43.4 |
| 67 | 10.0 | .0228 | 47.4 |
| 68 | 10.0 | .0930 | 64.4 |
| 69 | 10.0 | .0458 | 58.6 |
| 74 | 13.9 | .0116 | 42.2 |
| 76 | 13.9 | .0471 | 57.1 |
| 77 | 13.9 | .0948 | 66.2 |
| 42 | 18.2 | .0145 | 46.8 |
| 43 | 18.2 | .0291 | 51.5 |
| 44 | 18.2 | .0581 | 63.0 |
| 45 | 18.2 | .1159 | 75.0 |
| 70 | 22.4 | .0930 | 68.4 |
| 71 | 22.4 | .0458 | 58.3 |
| 72 | 22.4 | .0228 | 51.1 |
| 73 | 22.4 | 0.0114 | 44.4 |

# APPENDIX IV

## FORCED CIRCULATION THROUGH DROPS

## CALCULATION OF PSEUDO-FILM THICKNESS

### A. $SO_2$-$H_2O$ SYSTEM

$$x = AD_L c_s \frac{(1-F_2)}{(\Delta v_g/\Delta t)}$$

at 32.5°C

$c_s = 1.06 \times 10^{-3}$ mols $SO_2/cm.^3 H_2O$ [26]

$D_L = 2.10 \times 10^{-5}$ $cm.^2/sec.$ [38]

$r_d = 0.15$ cm. = drop radius = outside tube radius

$r_i = 0.028$ cm. = inside tube radius

The drop suspended on the hypodermic tubing had an equal height to width measurement, which was the same as the outside tip diameter. The area was estimated as being equal to the area of a sphere less the cross-sectional area of the outside tip. The true area may have been smaller, which would lead to smaller values of pseudo-film thickness and subsequently predict higher R values.

$$\text{Area} = A_{sphere} - A_{support} = 4\pi r_d^2 - \pi r_d^2 = 3\pi r_d^2$$

$$A = 3\pi(0.15)^2 = 0.212 \text{ cm.}^2$$

The outlet concentration $c_2 = \left(\frac{\Delta v_g}{\Delta t}\right) \frac{cm.^3 SO_2}{sec.} \left(\frac{1}{v_L}\right) \frac{sec.}{cm.^3 H_2O}$

$$x = (0.212)\text{cm.}^2(2.10 \times 10^{-5})\text{cm.}^2/\text{sec.}$$

$$\cdot(1.06 \times 10^{-3})\frac{\text{mols SO}_2}{\text{cm.}^3\ \text{H}_2\text{O}}\ \frac{(1-F_2)}{(\Delta v_g/\Delta t)}\ \frac{\text{sec.}}{\text{cm.}^3\ \text{SO}_2}$$

$$\cdot\left(\frac{305.5}{273}\right)(22,400)\frac{\text{cm.}^3}{\text{mol}} = 7.9 \times 10^{-5}\ \frac{(1-F_2)}{(\Delta v_g/\Delta t)}\ \text{cm.}$$

$$u_L = \frac{v_{H_2O}}{A_{\text{nozzle}}} = \frac{v_{H_2O}}{\pi(0.028)^2}\ \frac{\text{cm.}^3}{\text{cm.}^2} = 408\ v_{H_2O}\ \text{cm.}^2/\text{sec.}$$

This is the axial velocity and is considered as the maximum circulation velocity.

The average contact time is

$$t = \frac{\text{drop volume}}{\text{liquid flow rate}} = \frac{\frac{\pi}{6}(0.30)^3}{v_{H_2O}}\ \frac{\text{cm.}^3}{\text{cm.}^3/\text{sec.}}$$

$$= \frac{0.0142}{v_{H_2O}}\ \text{sec.}$$

The Reynolds Number $N_{Re} = \frac{d u_L \rho_L}{\mu_L}$

$d = 0.30$ cm.

$\rho_L = 0.995$ gm./cm.$^3$

$\mu_L = 0.760$ cps. $= 0.00760$ gm./cm.sec.

$$N_{Re} = \frac{(0.30)\text{cm.}(u_L)\text{cm./sec.}(0.995)\text{gm./cm.}^3}{(0.00760)\text{gm./cm.sec.}} = (39.3)u_L$$

The results are presented in Table 19.

## B. PROPYLENE GLYCOL-SO$_2$ SYSTEM

at 29.0°C $\quad c_s = 1.61 \times 10^{-3}\ \frac{\text{mols SO}_2}{1000\ \text{gm. Prop. Glycol}} \times 1.08\ \frac{\text{gm.}}{\text{cm.}^3}$

$= 1.74 \times 10^{-3}$ gm./cm.$^3$

$D_L = 0.94 \times 10^{-6}$ cm.$^2$/sec. (based on average conc.)

then, $$x = 0.57 \times 10^{-5} \frac{(1-F_s)}{(\Delta v_g/\Delta t)} \text{ cm.}$$

$$\rho_L = 1.03 \text{ gm./cm.}^3 \text{ at } C \simeq 0$$

$$\mu_L = 37.1 \text{ cps.} = 0.371 \text{ gm./cm.sec.}$$

$$N_{Re} = \frac{(0.30)(u_L)(1.03)}{(0.371)} = (0.833)u_L$$

The results are presented in Table 20.

## TABLE 19

## FORCED CIRCULATION THROUGH $H_2O$ DROPS

**Glass nozzle = 0.56 mm. I.D. internal tube, 3 mm. O.D. external tube**

**Drop size:** 3 mm. diameter

**Temperature:** 32.5°C

| Liq. Rate | t | $\Delta v_g$ | $\frac{\Delta v_g}{\Delta t}$ | $C_2 \times 10^4$ |
|---|---|---|---|---|
| $\frac{cm.^3}{sec.}$ | sec. | $cm.^3$ | $\frac{cm.^3}{sec.}$ | $\frac{mols}{cm.^3 H_2O}$ |
| 0.001 | 960 | 3.0 | 0.00312 | 1.25 |
| .0045 | 480 | 4.0 | .00835 | 0.74 |
| .0083 | 711 | 12.5 | .0176 | .85 |
| .0090 | 273 | 5.0 | .0183 | .81 |
| .016 | 631 | 17.5 | .0277 | .69 |
| .020 | 372 | 10.0 | .0269 | .54 |
| .025 | 245 | 10.0 | .041 | .66 |
| .0295 | 458 | 20.0 | .0436 | .59 |
| .0385 | 171 | 10.0 | .0585 | .61 |
| .051 | 300 | 20.0 | .0667 | .52 |
| .058 | 273 | 20.0 | .0733 | .51 |
| 0.058 | 423 | 25.0 | 0.0591 | 0.41 |

TABLE 19—Continued

| $F_2$ | $\frac{(1-F_2)}{(\Delta v_g/\Delta t)}$ | x | $\frac{3r}{x}$ | $u_L$ | $N_{Re}$ |
|---|---|---|---|---|---|
| | | cm. | | $\frac{cm.}{sec.}$ | |
| 0.118 | 295 | 0.0348 | 12.9 | 0.408 | 16.0 |
| .070 | 111 | .0131 | 34.3 | 1.83 | 71.9 |
| .080 | 52.3 | .00618 | 72.9 | 3.38 | 133. |
| .076 | 50.6 | .00597 | 75.3 | 3.67 | 144. |
| .065 | 33.7 | .00397 | 113. | 6.52 | 256. |
| .051 | 35.3 | .00417 | 108. | 8.16 | 321. |
| .062 | 22.9 | .00270 | 167. | 10.2 | 401. |
| .056 | 21.6 | .00255 | 176 | 12.0 | 471. |
| .058 | 16.1 | .00190 | 237. | 15.7 | 616. |
| .049 | 14.3 | .00169 | 264. | 20.8 | 816. |
| .048 | 13.0 | .00153 | 294. | 23.7 | 931. |
| 0.039 | 16.3 | 0.00192 | 234. | 23.7 | 931. |

## TABLE 20

## FORCED CIRCULATION THROUGH PROPYLENE GLYCOL DROPS

Glass nozzle = 0.56 mm. I.D. internal tube, 3mm O.D. external tube

Drop size: 3 mm. diameter

Temperature: 29.0°C

| Liq. Rate | $t$ | $\Delta v_g$ | $\frac{\Delta v_g}{\Delta t}$ | $C_2 \times 10^5$ |
|---|---|---|---|---|
| $\frac{cm.^3}{sec.}$ | sec. | $cm.^3$ | $\frac{cm.^3}{sec.}$ | $\frac{mols}{cm.^3}$ |
| 0.011 | 360 | 2.5 | 0.00695 | 2.55 |
| .016 | 630 | 4.0 | .00635 | 1.60 |
| .030 | 390 | 3.5 | .0090 | 1.21 |
| .039 | 256 | 4.0 | .0156 | 1.61 |
| .049 | 360 | 4.0 | .0111 | 0.91 |
| .066 | 170 | 2.5 | .0147 | 0.90 |
| 0.075 | 250 | 5.0 | 0.0200 | 1.07 |

TABLE 20—Continued

| $F_2$ | $\frac{(1-F_2)}{(\Delta v_g/\Delta t)}$ | $x$ | $\frac{3r}{x}$ | $u_L$ | $N_{Re}$ |
|---|---|---|---|---|---|
| | | cm. | | $\frac{\text{cm.}}{\text{sec.}}$ | |
| 0.0146 | 141 | 0.0121 | 37.2 | 4.49 | 3.74 |
| .0092 | 156 | .0134 | 33.6 | 6.53 | 5.45 |
| .0070 | 110 | .0095 | 47.3 | 12.3 | 10.3 |
| .0093 | 64 | .0055 | 82 | 15.9 | 13.3 |
| .0052 | 90 | .0077 | 58 | 20.0 | 16.7 |
| .0052 | 68 | .0059 | 76 | 26.9 | 22.4 |
| 0.0062 | 50 | 0.0043 | 105 | 30.6 | 25.5 |